NASA Conference Publication 2427

Structural Ceramics

Proceedings of a workshop sponsored by
NASA Lewis Research Center
Cleveland, Ohio
May 20–21, 1986

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NASA
National Aeronautics
and Space Administration

Scientific and Technical
Information Branch

1986

PREFACE

Welcome to Lewis Research Center and the Materials Division. We are very pleased that you could visit us and hear about all the progress we, our contractors, and grantees have been making in ceramics. We feel ceramics and ceramic matrix composites are an exciting area of tailored structural materials research. NASA has made a strong commitment to advance this technology and we will work with U.S. industry to foster our national position in world markets. In fact, that is the job of the Materials Division in all areas of NASA technology needs.

If any of your organizations are interested in more detailed information on our programs, in joint research efforts, or in sending a research here for some extended on-site studies, feel free to call me and we will discuss it.

Sal Grisaffe

Chief, Materials Division

(216) 433-3193

CONTENTS

CERAMICS FOR TURBINE ENGINES

Stanley R. Levine

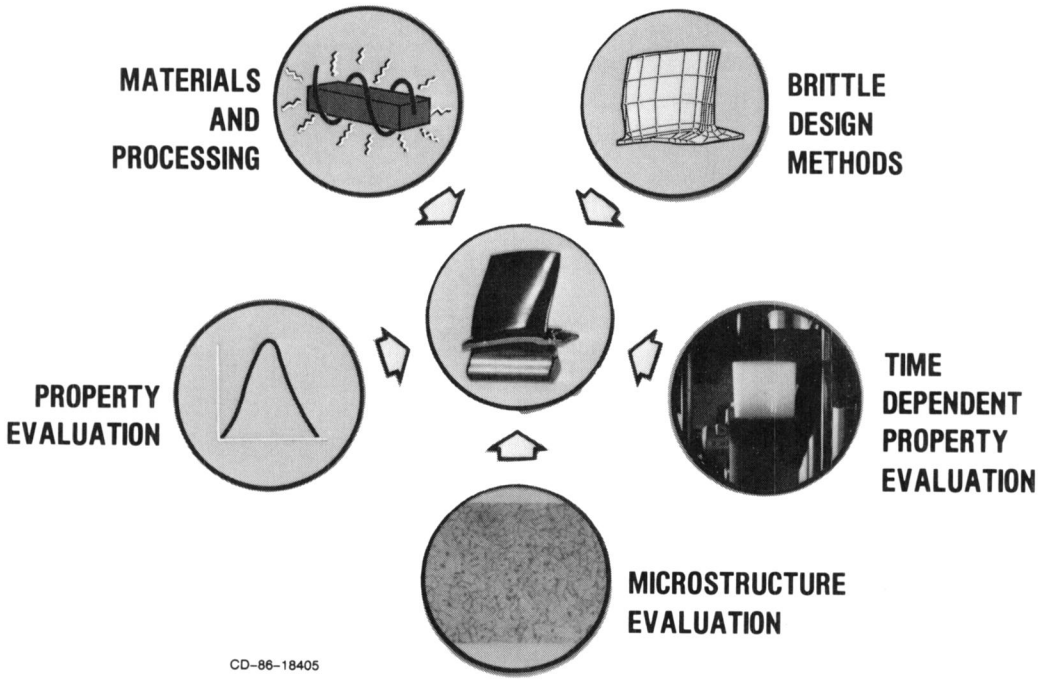
NASA Lewis Research Center
Cleveland, Ohio 44135

The Ceramics for Turbine Engines Project is comprised of three main research thrusts with major elements as indicated:

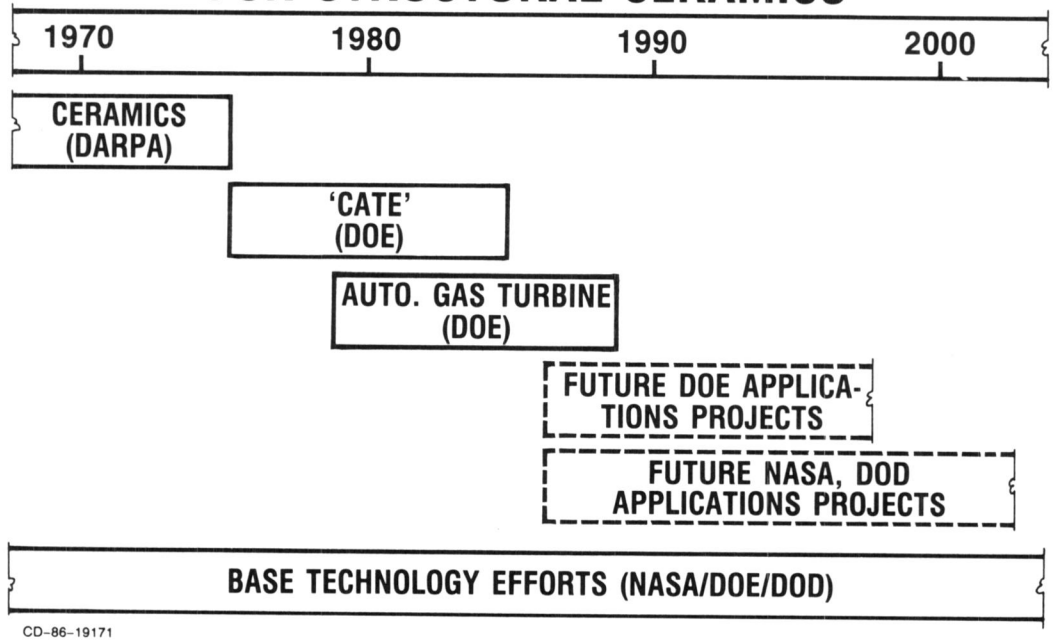
- Materials and Processing
  - Monolithics
  - Fiber reinforced
- Design Methodology
  - Design code
  - Tribology
- Life Prediction
  - Environmental effects
  - Non-destructive evaluation
  - Fracture and fatigue
  - Time dependent behavior

The overall objective of this program is to provide the ceramics technology base in materials and structures for aerospace propulsion and power applications programs. The effort is complementary to and coordinated with the Department of Energy funded Ceramic Technology for Advanced Heat Engines Project at Oak Ridge National Laboratory. From the NASA perspective an enhanced ceramics technology base directly supports aeronautics initiatives in small engine technology, high-performance turbine engine technology, and hypersonics. The Ceramics for Turbine Engines Project is funded at about $2M per year and involves about 20 researchers in the Materials Division and the Structures Division at Lewis as well as contract and grant research. An overview of the program, which includes the technical objectives and content of each thrust, is provided in the following figures. This workshop reports on research efforts funded mainly by Ceramics for Turbine Engines. A major strength of the program is the increasingly interdisciplinary nature of the research being carried out in-house. Several of the papers presented will illustrate and demonstrate the benefits of such an approach.

CERAMICS FOR TURBINE ENGINES



GOVERNMENT-SPONSORED TECHNOLOGY PROGRAMS FOR STRUCTURAL CERAMICS



DOE/NASA ADVANCED GAS TURBINE TECHNOLOGY DEVELOPMENT PROJECT

OBJECTIVE

- DEVELOP A TECHNOLOGY BASE APPLICABLE TO A COMPETITIVE AUTOMOTIVE GAS TURBINE ENGINE

TECHNOLOGY DEVELOPMENT GOALS

- 30% IMPROVEMENT IN FUEL ECONOMY OVER A CONVENTIONAL (SI) ENGINE IN A 3000 LB VEHICLE
- ADAPTABILITY TO ALTERNATIVE FUELS
- MEET OR EXCEED PRESENT EMISSION STANDARDS
- COMPETITIVE RELABILITY, LIFE, AND COSTS

APPROACH

- TWO ENGINE/AUTOMOBILE CONTRACTOR TEAMS (GARRETT/FORD AND ALLISON/PONTIAC)
  - DESIGN, FABRICATE, AND TEST ALL-CERAMIC HOT SECTION COMPONENTS
- SUPPORTING RESEARCH AND TECHNOLOGY EFFORT IN CRITICAL AREAS
- INITIATED 1980--PLANNED COMPLETION 1986

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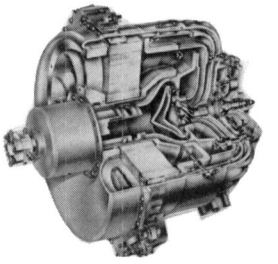

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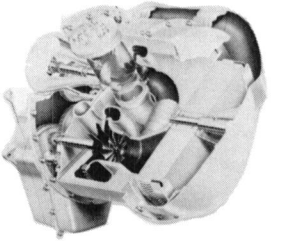

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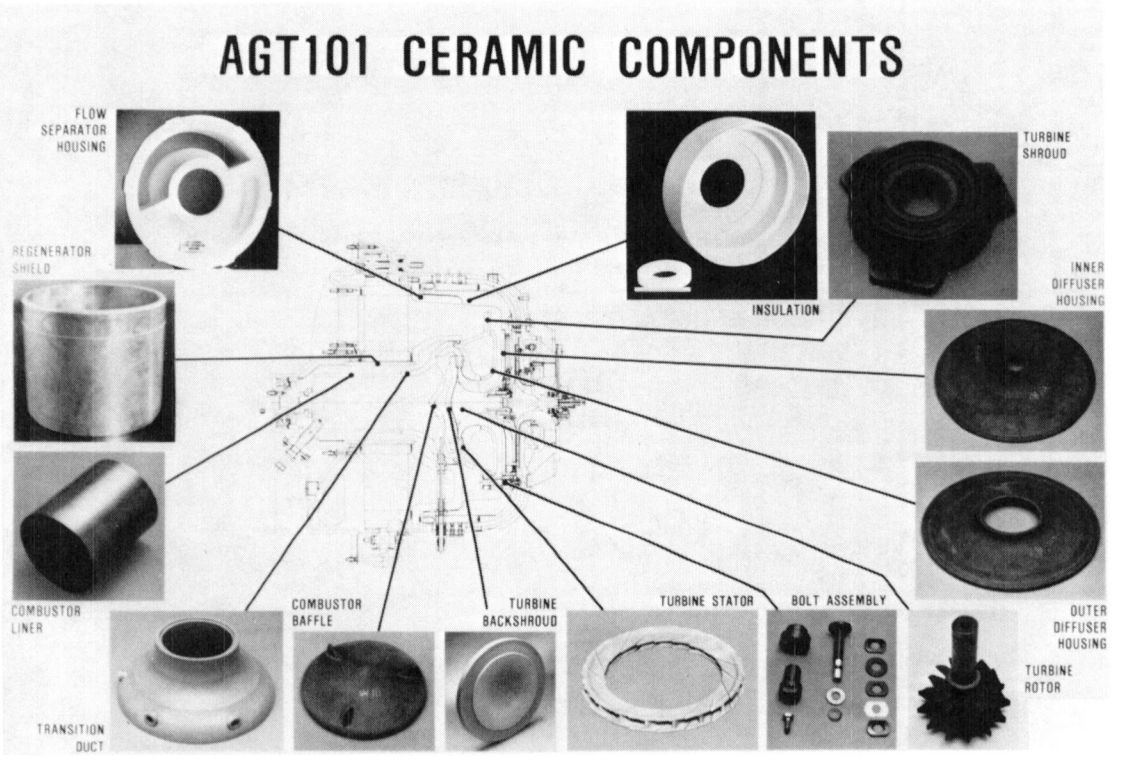
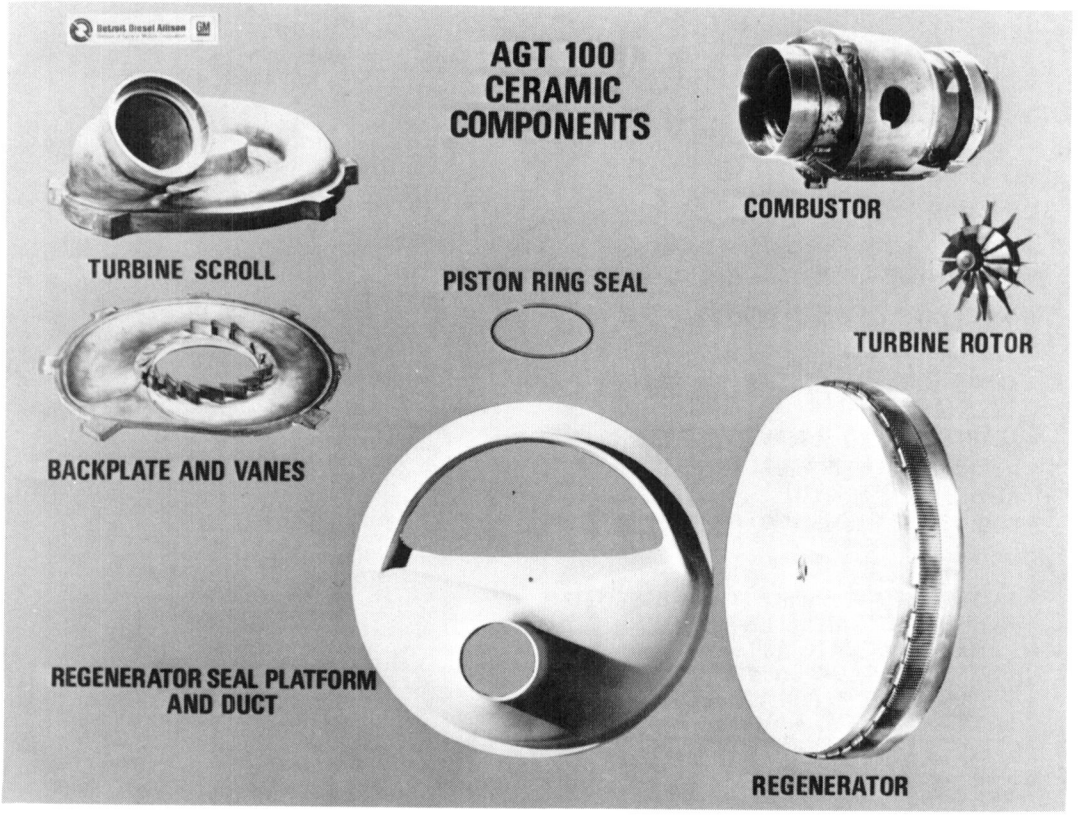




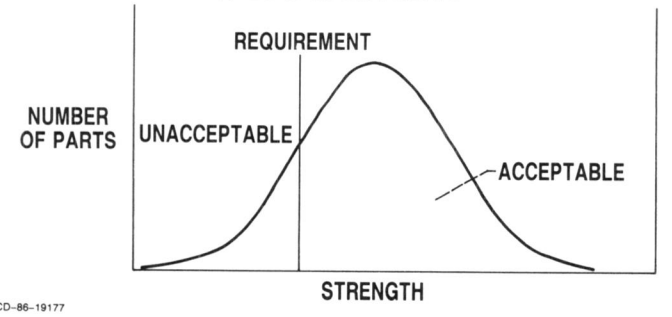
STATUS OF MONOLITHIC CERAMIC MATERIALS

CERAMIC MATERIALS HAVE DEMONSTRATED:

- ★ GOOD HIGH TEMPERATURE STRENGTH
- ★ GOOD OXIDATION RESISTANCE
- ★ GOOD EROSION RESISTANCE
- ★ NET SHAPE FABRICATION CAPABILITY

BUT

- ★ LOW RELIABILITY



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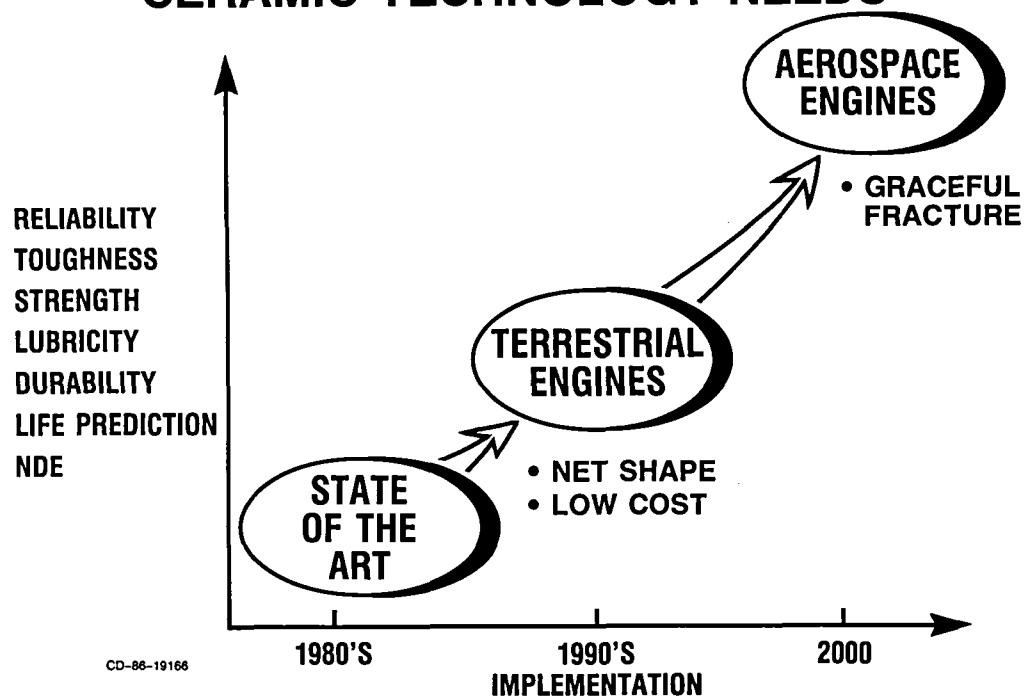
CERAMIC TECHNOLOGY NEEDS



STRATEGIC THRUSTS IN AERONAUTICS TO ESTABLISH TECHNOLOGY FOR 21st CENTURY ADVANCED AIRCRAFT

NASA OAST/AERONAUTICS - NOVEMBER 1984

PRESIDENTIAL SCIENCE ADVISOR KEYWORTH - APRIL 1985

- DEVELOP ESSENTIAL TECHNOLOGIES FOR HIGH-EFFICIENCY SUBSONIC TRANSPORTS.
- ESTABLISH TECHNOLOGY READINESS FOR EFFICIENT SUPERSONIC CRUISE TRANSPORT AND FIGHTER/ATTACK AIRCRAFT.
- DEVELOP ESSENTIAL TECHNOLOGIES FOR REALIZATION OF PRACTICAL HYPERSONIC AND TRANSATMOSPHERIC FLIGHT AIRCRAFT.

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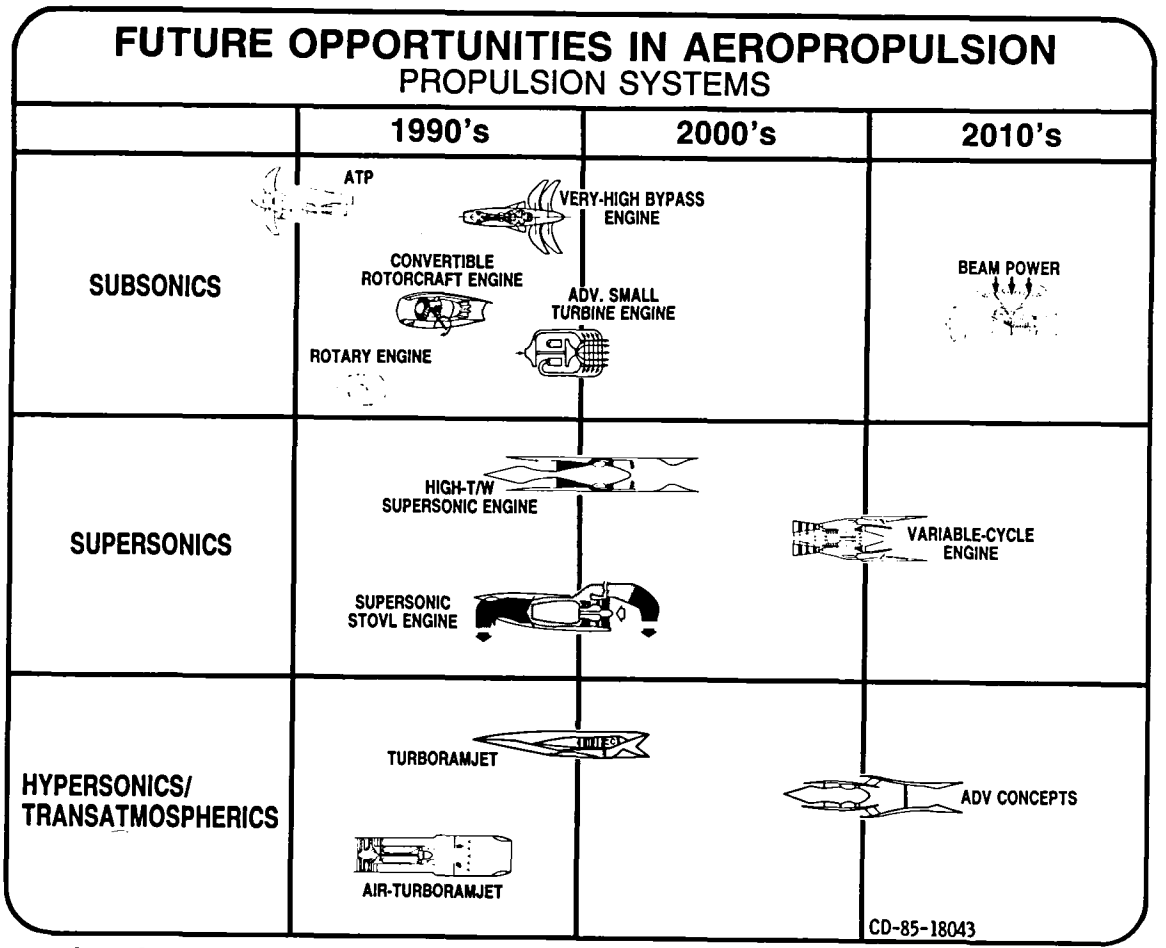
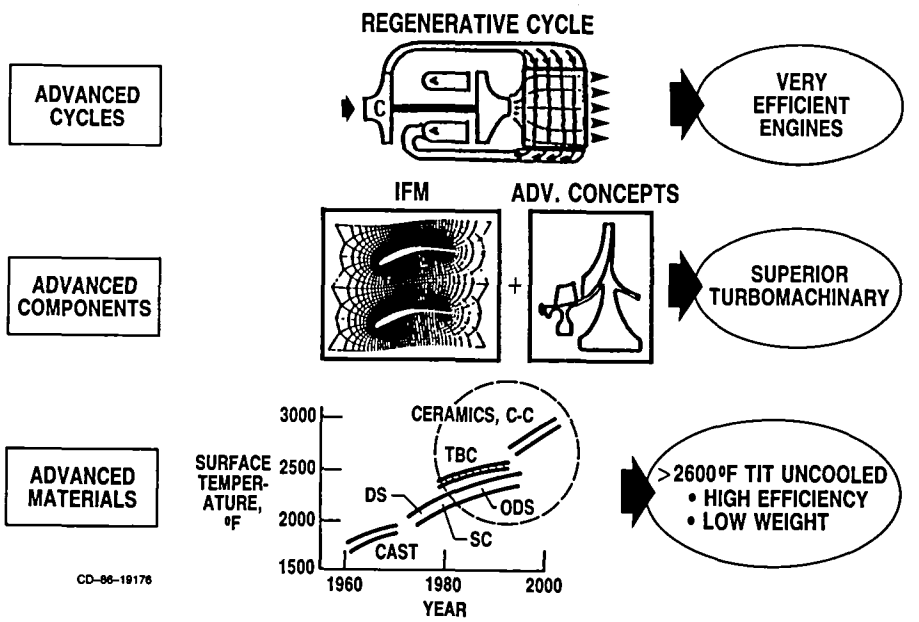
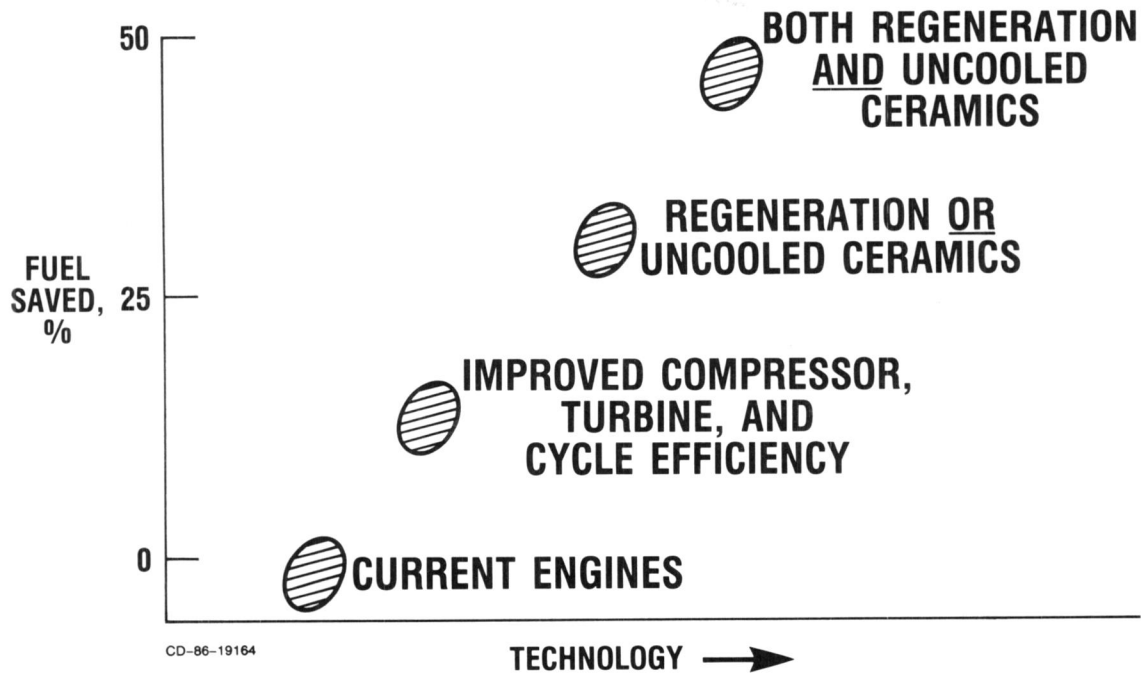


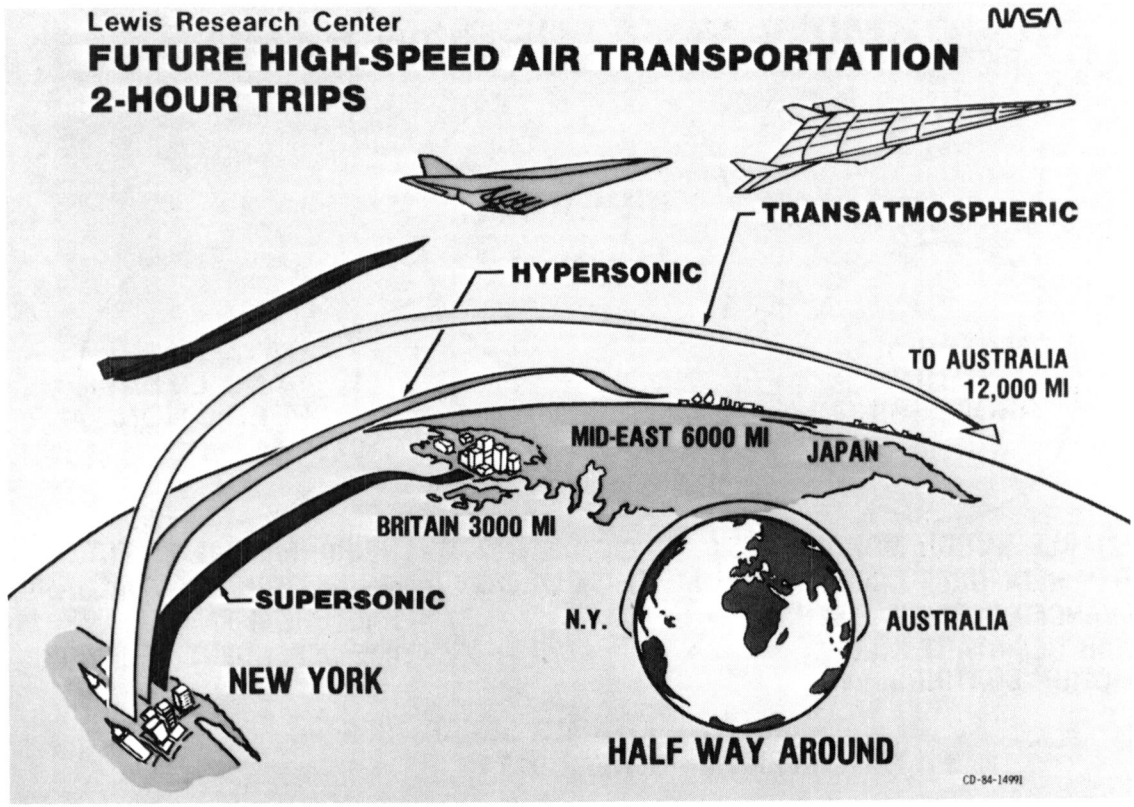
SMALL ENGINE TECHNOLOGY OPPORTUNITIES



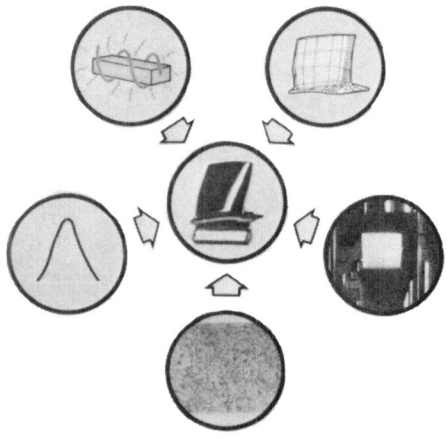
TECHNOLOGY BENEFITS FROM CERAMICS

TYPICAL-COMMUTER MISSION





CERAMICS FOR TURBINE ENGINES



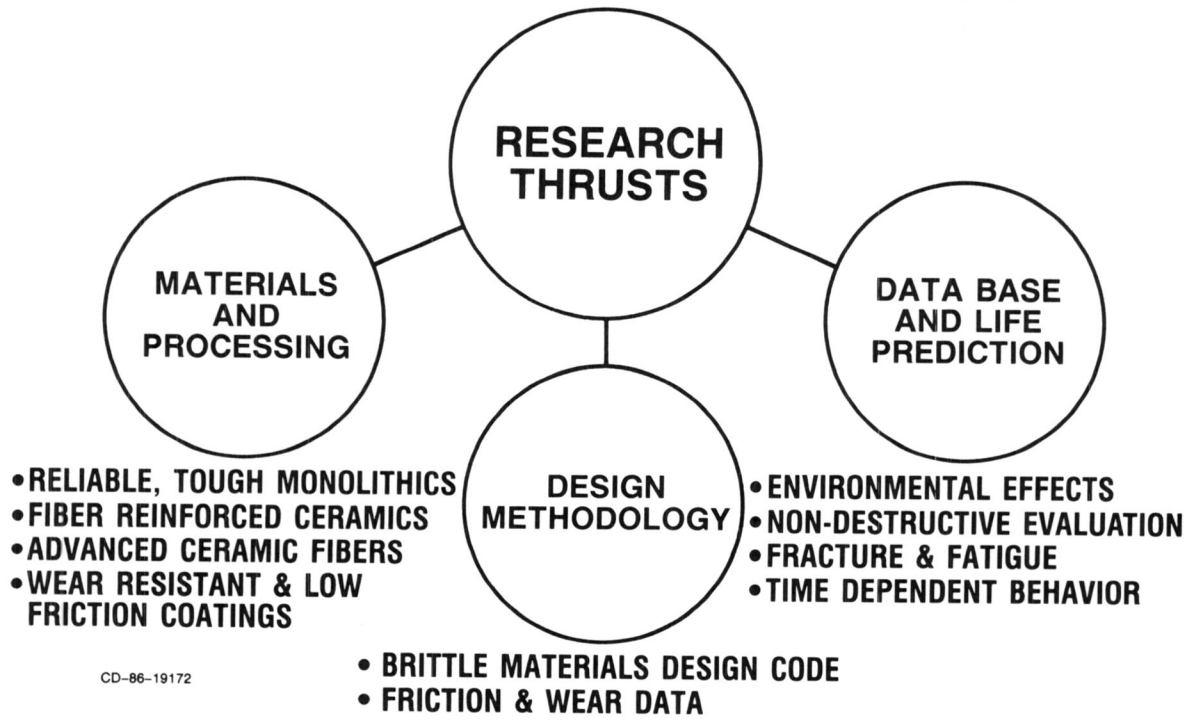
OBJECTIVE

DEVELOP THE TECHNOLOGY REQUIRED TO IMPROVE STRUCTURAL CERAMIC RELIABILITY AND PERMIT USE OF CERAMICS IN ADVANCED HEAT ENGINES

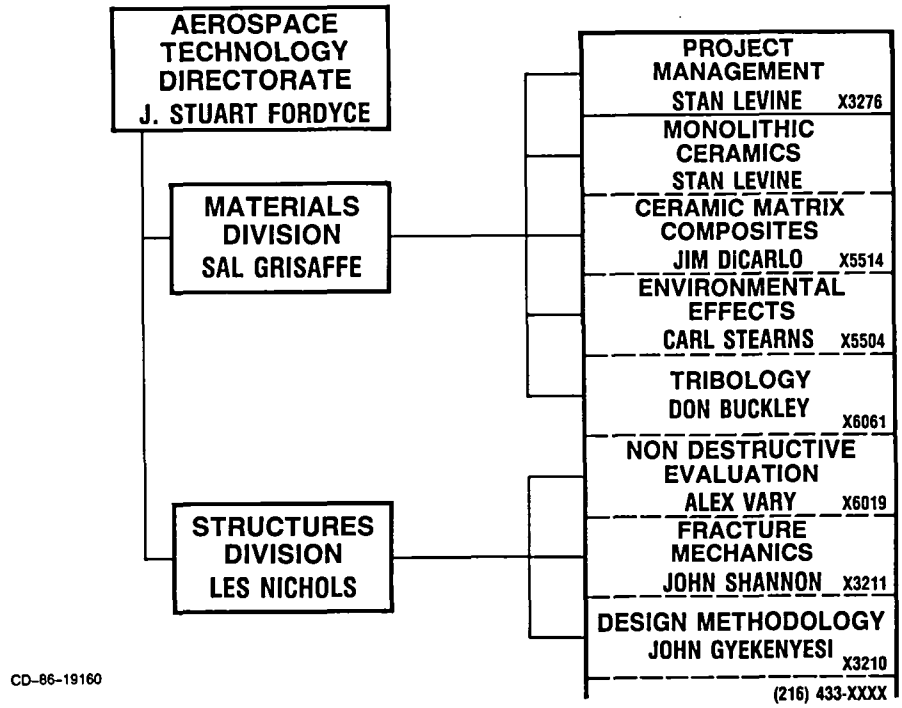
APPROACHES

- MATERIALS AND PROCESSING
- DESIGN METHODOLOGY
- LIFE PREDICTION

CERAMICS FOR TURBINE ENGINES



CERAMICS FOR TURBINE ENGINES
PROJECT TEAM



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CERAMICS FOR TURBINE ENGINES

MATERIALS & PROCESSES

- MONOLITHICS
  - SUNIL DUTTA
  - MARC FREEDMAN
  - TOM HERBELL
  - JANET HURST
  - DOUG KISER
  - BILL SANDERS
  - NANCY SHAW
- COMPOSITES
  - NAROTTAM BANSAL
  - DON BEHRENDT
  - RAM BHATT
  - JIM DiCARLO
  - GARY HALLUM
  - FRAN HURWITZ
  - MARK HYATT
  - MARTHA JASKOWIAK
  - WARREN PHILIPP

DESIGN METHODOLOGY

- DESIGN
  - JOHN GYEKENYESI
  - NOEL NEMETH
- TRIBOLOGY
  - DAN DEADMORE
  - DON BUCKLEY
  - KAY MIYOSHI
  - HAL SLINEY

LIFE PREDICTION

- CORROSION
  - DENNIS FOX
  - NATE JACOBSON
  - JIM SMIALEK
  - CARL STEARNS
- NDE
  - GEORGE BAAKLINI
  - ED GENERAZIO
  - STAN KLIMA
  - DON ROTH
  - ALEX VARY
- FRACTURE MECH.
  - RAY BUBSEY
  - ANTHONY CALOMINO
  - JON SALEM
  - JOHN SHANNON

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LEWIS CERAMICS CAPABILITIES

FIBERS

FIBER COATING
HIGH TEMPERATURE FIBER TESTING
FIBER PHYSICAL/MECHANICAL PROPERTIES

CERAMIC/CERAMIC COMPOSITE FABRICATION

FIBER/MATRIX TAPE FAB
HOT PRESS
REACTION BONDING
HOT ISOSTATIC PRESS (2200 °C, 20 ksi)
HIGH PRESSURE N_2 SINTERING (2150 °C, 1000 psi)
CVD & CVI FABRICATION
SOL GEL PROCESSING/CHARACTERIZATION
POLYMER PROCESSING/CHARACTERIZATION
POWDER PROCESSING/CHARACTERIZATION

INTERDISCIPLINARY COLLABORATION

ENVIRONMENTAL EFFECTS - BURNER RIGS, H_2/O_2 RIG, COATINGS
NDE - RADIOGRAPHY ACOUSTIC MICROSCOPY, ULTRASONICS
FRACTURE MECHANICS & FATIGUE
STRUCTURAL ANALYSIS & DESIGN METHODOLOGY
SURFACE SCIENCE - FRICTION, WEAR, COATINGS

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CERAMICS FOR TURBINE ENGINES

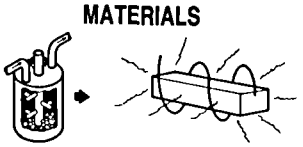
—MATERIALS AND PROCESSING—

OBJECTIVE:

IMPROVE RELIABILITY, STRENGTH AND TOUGHNESS OF CERAMICS/CERAMIC MATRIX COMPOSITES

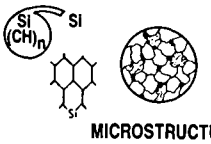
APPROACH:

POWDER DERIVED MATERIALS



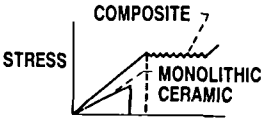
POWDER PROCESSING SINTERING

CHEMICALLY DERIVED MATERIALS



MICROSTRUCTURE

COMPOSITES

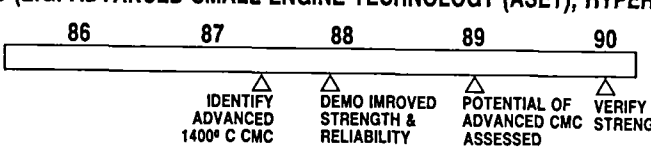


STRONGER, TOUGHER CERAMICS	CONTROLLED PROPERTIES MICROSTRUCTURES & MODELS	FIBER REINFORCED CERAMICS
IMPROVE RELIABILITY	QUANTIFY PROGRESS & DEFINE NEW OPTIONS	IMPROVE STRENGTH, TOUGHNESS & PROVIDE GRACEFUL FRACTURE

BENEFITS:

ADVANCED CERAMIC MATERIALS TECHNOLOGY FOR AEROSPACE PROPULSION AND POWER APPLICATIONS (E.G. ADVANCED SMALL ENGINE TECHNOLOGY (ASET), HYPERSONICS)

SCHEDULE:



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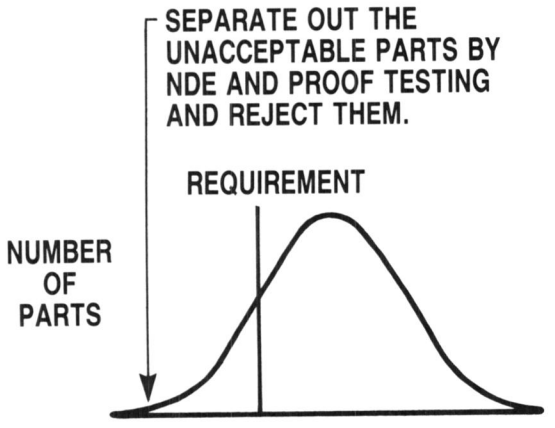
APPROACHES TO CERAMIC RELIABILITY

"INSPECT-IN" THE QUALITY



- INEFFICIENT
- COSTLY

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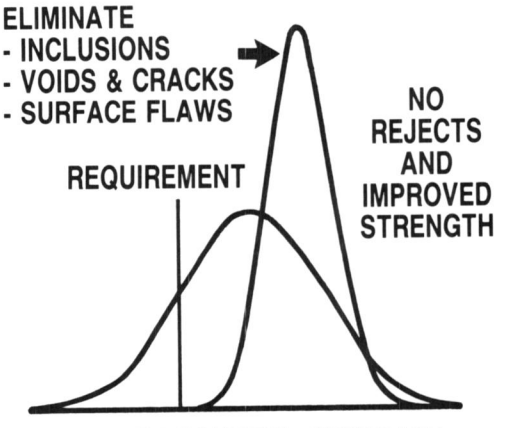
IMPROVE THE PROCESS



QUALITY CONTROL APPROACH

- EFFICIENT
- LOW COST
- RELIABLE

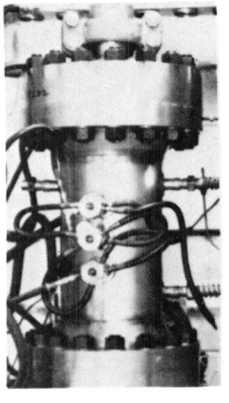
MONOLITHIC CERAMICS

OBJECTIVES:

- UNDERSTAND MICROSTRUCTURE/PROCESSING/ PROPERTIES/RELATIONSHIPS
- IMPROVE RELIABILITY

APPROACHES

SINTERING/HIGH P_{N_2} HIP

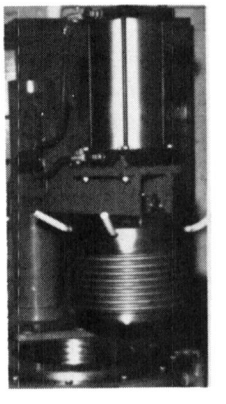


SINTERED Si_3N_4 (SSN)

REACTION BONDED Si_3N_4 (RBSN)

SINTERED REACTION BONDED Si_3N_4 (SRBSN)

SINTERED SiC (SSC)



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FIBER REINFORCED CERAMICS APPROACH TO RELIABILITY

INCORPORATE CONTINUOUS CERAMIC FILAMENTS HAVING GREATER STIFFNESS THAN MATRIX

- **ADVANTAGES**
  - IMPROVED TOUGHNESS IMPARTED BY CRACK DEFLECTION AND CRACK BRIDGING
  - INCREASED MODULUS AND STRESS TO FAILURE
  - "METAL-LIKE" STRESS-STRAIN BEHAVIOR
  - GRACEFUL FAILURE
- **DISADVANTAGES**
  - PROCESSING MORE DIFFICULT
  - AVAILABLE FIBERS LIMITED
  - CONTROL OF FIBER-MATRIX BOND REQUIRED

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CERAMICS FOR TURBINE ENGINES

—DESIGN METHODOLOGY—

OBJECTIVES:

- DEVELOP AND VERIFY MECHANICAL DESIGN METHODS FOR CERAMIC AND CERAMIC COMPOSITE COMPONENTS
- UNDERSTAND FRICTION/WEAR INTERACTIONS AND DEVELOP HIGH TEMPERATURE SOLID FILM AND COMPOSITE LUBRICANT TECHNOLOGY

APPROACH:

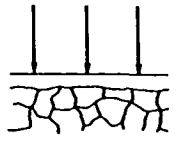
DESIGN METHODS

RADIAL TURBINE BLADE DISC SECTOR ANALYSIS

CERAMIC BLADE-DISC FINITE ELEMENT MODEL

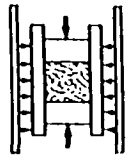
TRIBOLOGY

PLASMA SPRAY & VAPOR DEPOSITION



NEW SURFACE FILMS AND COATINGS

PRESSURE

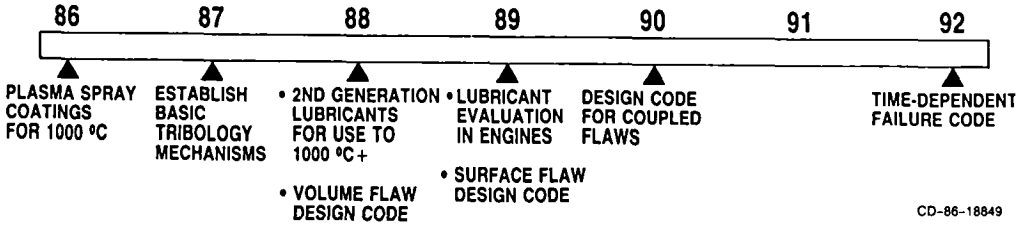


NEW SELF-LUBRICATING CERAMIC COMPOSITES

BENEFITS:

ENABLING TECHNOLOGY TO PERMIT USE OF CERAMIC MATERIALS IN ADVANCED AEROSPACE PROPULSION AND POWER SYSTEMS

SCHEDULE: AT GL



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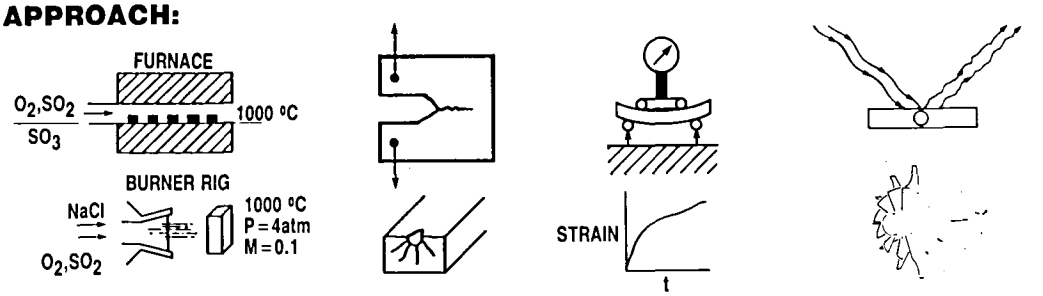
CERAMICS FOR TURBINE ENGINES

—LIFE PREDICTION—

OBJECTIVE:

DEVELOP LIFE PREDICTION AND RELIABILITY ASSESSMENT TOOLS FOR STRUCTURAL CERAMICS

APPROACH:



CORROSION MECHANISMS AND CONTROL STRATEGIES

FRACTURE MECHANICS

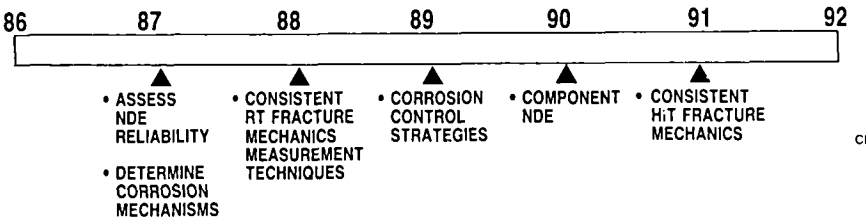
TIME DEPENDENT BEHAVIOR

NON-DESTRUCTIVE EVALUATION AND PROOF TEST

BENEFITS:

- ENABLING TECHNOLOGY TO PERMIT RELIABLE DESIGN AND USE OF ADVANCED CERAMIC MATERIALS
- GUIDE DEVELOPMENT OF DURABLE CERAMICS FOR AEROSPACE PROPULSION AND POWER SYSTEMS

SCHEDULE:



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FUTURE OPPORTUNITIES FOR CERAMICS

SYSTEMS	MATERIAL NEEDS	OPPORTUNITY
• VEHICULAR AND STATIONARY POWER • ADVANCED SMALL ENGINE TECHNOLOGY (ASET)	• HIGH-TEMPERATURE, NON-STRATEGIC MATERIALS AT LOW COST (2500 °F) • VERY HIGH RELIABILITY, TOUGHNESS AND STRENGTH-TO-WEIGHT (2700 °F) • ADVANCED RECUPERATORS/REGENERATORS (2200 °F) • ASSEMBLY OF CERAMICS INTO A WORKABLE ENGINE SYSTEM	• CONTINUE EMPHASIS ON RELIABILITY • DEVELOP THERMALLY STABLE 10 TO 25 μ DIAMETER CERAMIC FIBER AND APPLY IN CERAMIC MATRIX COMPOSITES • DEVELOP AND VERIFY POTENTIAL OF ADVANCED MATERIALS • ADVANCED JOINING, NONJOINING AND CONTACT STRESS CONTROL TECHNOLOGY
• HIGH-THRUST-TO-WEIGHT ENGINES (HPTE) • AEROSPACEPLANE	• VERY HIGH RELIABILITY, TOUGHNESS AND STRENGTH-TO-WEIGHT (3000 °F) • SAME AS HPTE (3000 °F++) • DURABLE CERAMICS FOR USE IN 0° AT HIGH HEAT FLUX (EDGE INSERTS) AND IN H_2/O_2 (ENGINE SEALS)	• DESIGN AND LIFE PREDICTION • FIBERS AND COMPOSITES • FIBERS AND COMPOSITES • IDENTIFY SUITABLE MATERIALS

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FRICTION AND WEAR OF CERAMICS

Donald H. Buckley
NASA Lewis Research Center

The adhesion, friction, wear, and lubricated behaviors of both oxide and non-oxide ceramics are reviewed. Ceramics are examined in contact with themselves, other harder materials, and metals. Elastic, plastic, and fracture behavior of ceramics in solid state contact is discussed. The contact load necessary to initiate fracture in ceramics is shown to be appreciably reduced with tangential motion. Both friction and wear of ceramics are anisotropic and relate to crystal structure as with metals. Grit size effects in two- and three-body abrasive wear are observed for ceramics. Both the free energy of oxide formation and the d valence bond character of metals are related to the friction and wear characteristics for metals in contact with ceramics. Surface contaminants affect friction and adhesive wear. For example, carbon on silicon carbide and chlorine on aluminum oxide reduce friction while oxygen on metal surfaces in contact with ceramics increases friction. Lubrication increases the critical load necessary to initiate fracture of ceramics both in indentation and with sliding or rubbing.

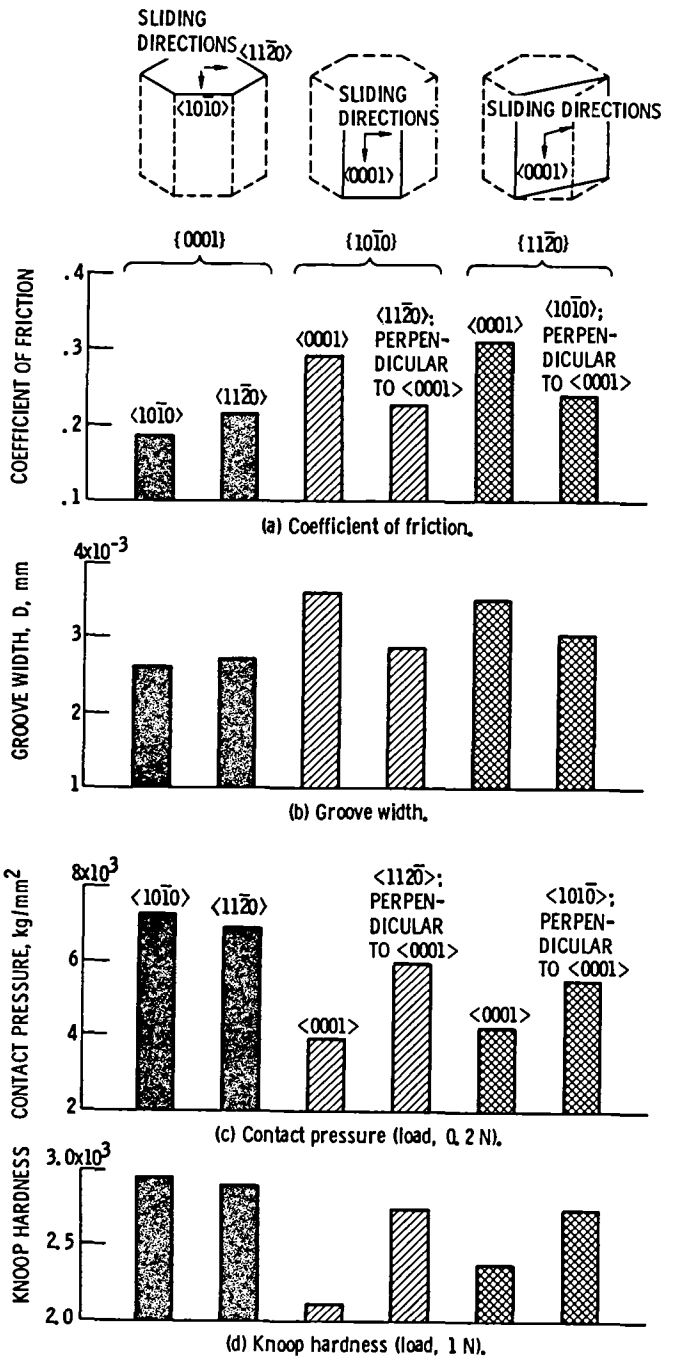


Figure 1. - Anisotropies on {0001}, {10$\bar{1}$0}, and {11$\bar{2}$0} surfaces of SiC.

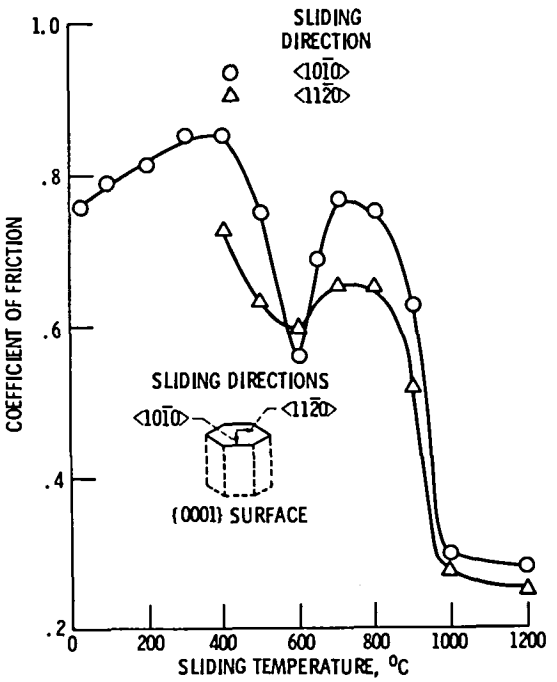


Figure 2. - Effect of temperature on coefficient of friction for silicon carbide {0001} surface sliding against an iron rider. The iron rider was argon ion sputter cleaned before experiments. Normal load, 0.2 N, vacuum, 10 nPa.

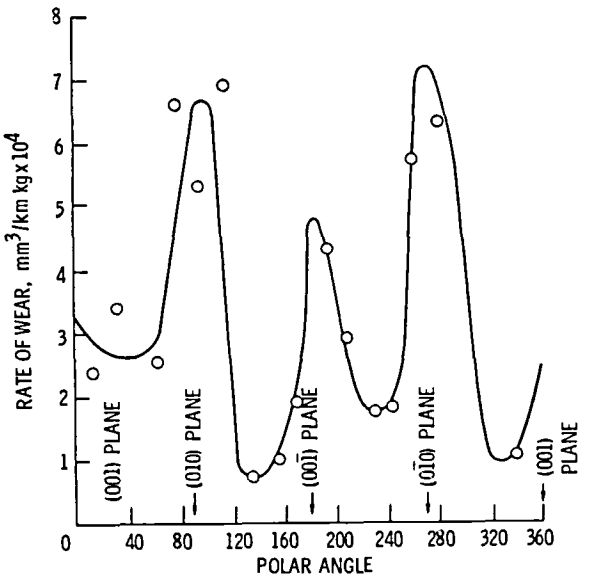


Figure 3. - Rate of wear of a rutile single-crystal sphere on a great circle in the plane of the a- and c-axes is normal to plane of sliding at 0 and 180°. Slide direction in plane of the great circle (ref. 8).

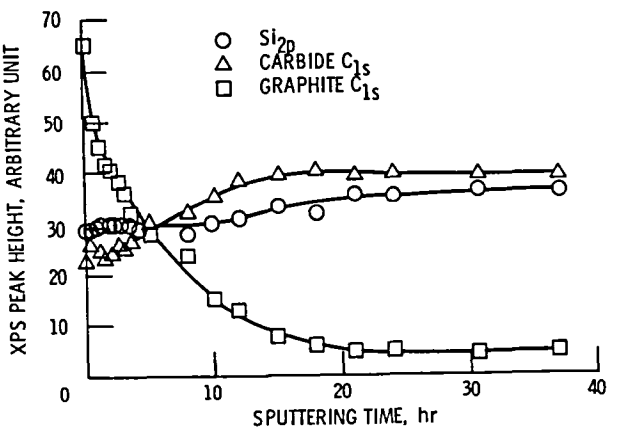
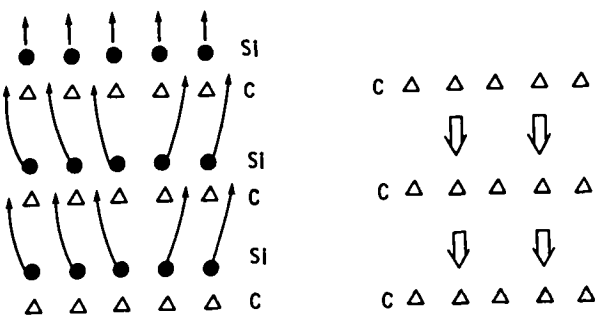


Figure 4. - Elemental depth profile of silicon carbide {0001} surface preheated a temperature of 1500° C for 1 hour.



(a) Evaporation of silicon. (b) Collapse of carbon.

Figure 5. - Graphitization of silicon carbide surface.

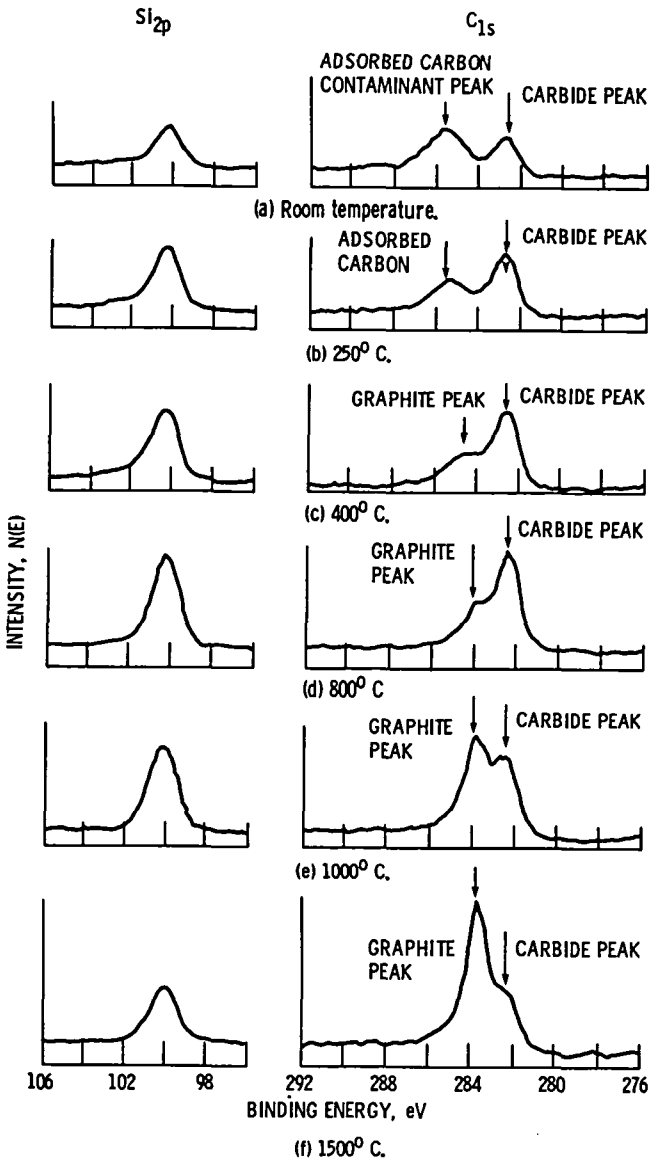


Figure 6. - Representative Si_{2p} and C_{1s} XPS peaks on silicon carbide {0001} surface preheated at various temperatures to 1500° C.

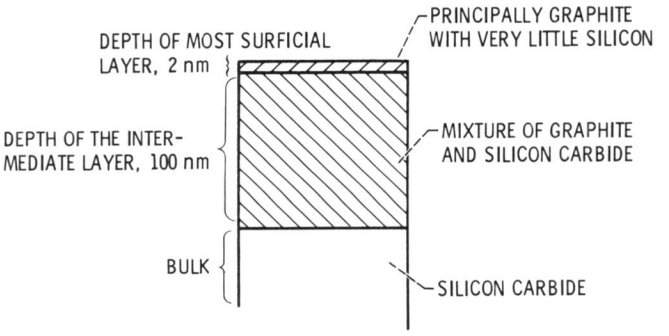


Figure 7. - Surface condition of silicon carbide after heating at temperatures above 1200° C.

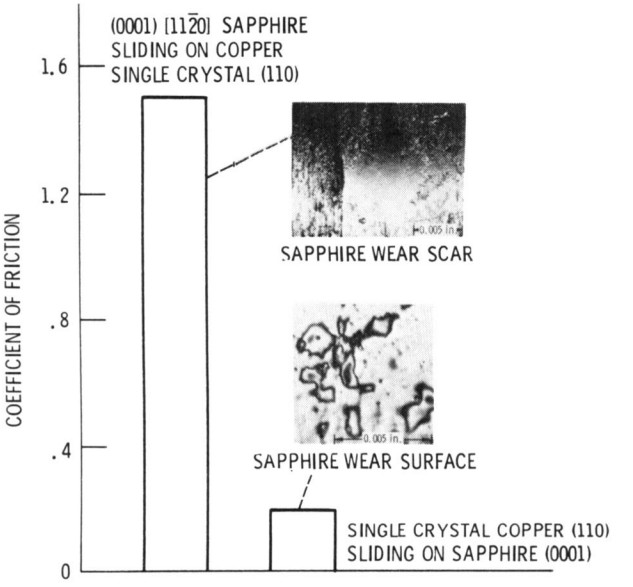


Figure 8. - Friction for copper in sliding contact with sapphire in vacuum 30 nPa; load, 100 g; sliding velocity, 0.013 cm/s.

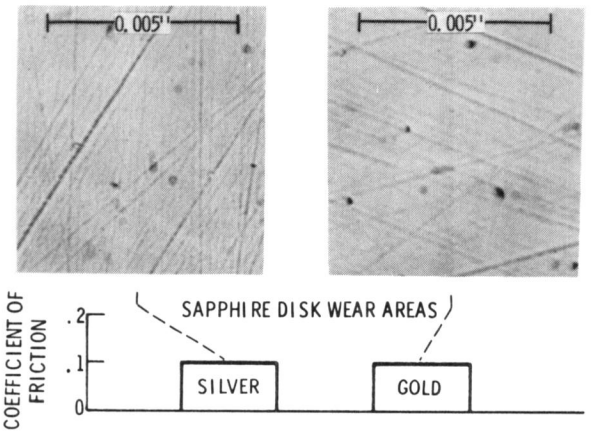


Figure 9. - Coefficient of friction for gold and silver riders sliding on sapphire in vacuum (30 nPa). Sliding velocity, 0.013 cm/s; ambient temperature, 25° C; duration, 1hr.

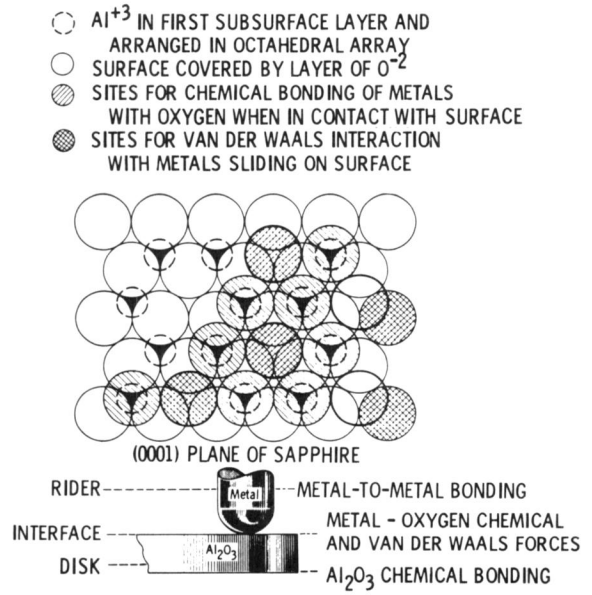


Figure 10. - Nature of surface interaction and bonding of metal to Al_2O_3.

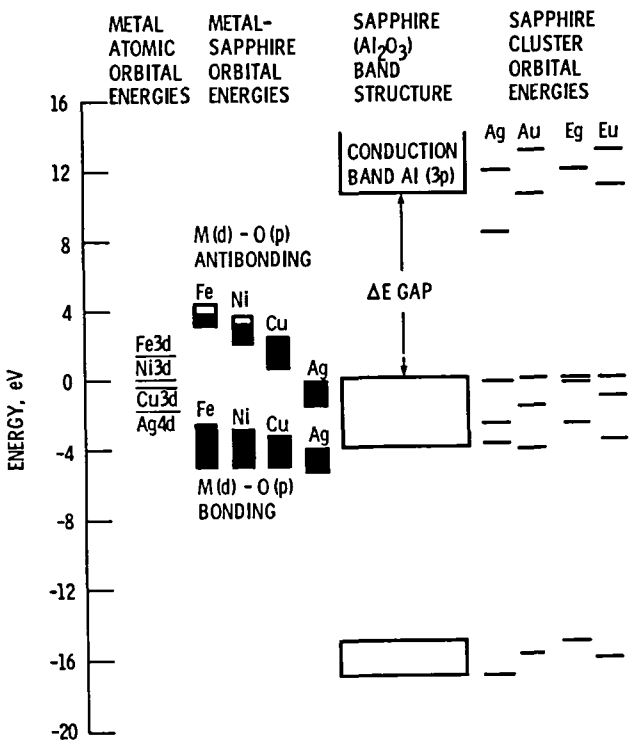
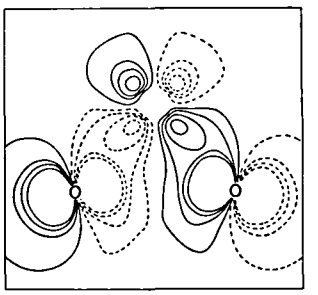
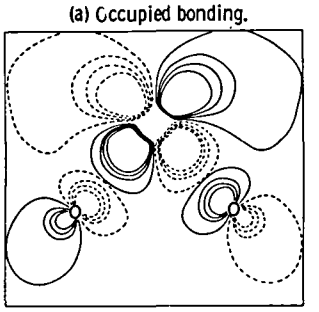


Figure 11. - Molecular-orbital energies, as determined by the self-consistent-field X-alpha scattered wave method, for clusters representing bulk sapphire and metal-sapphire interfaces

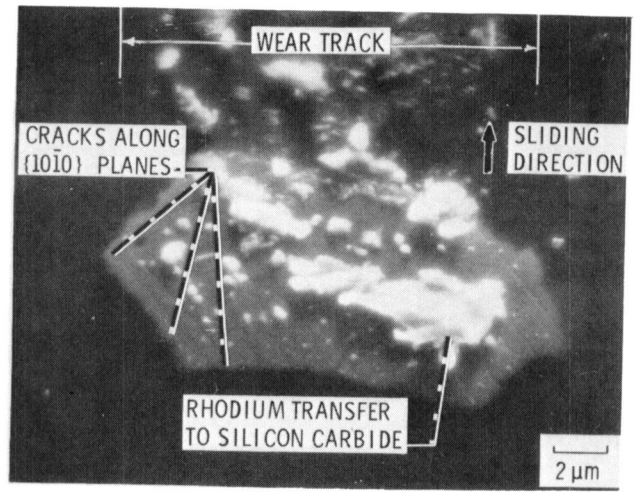


(a) Occupied bonding.

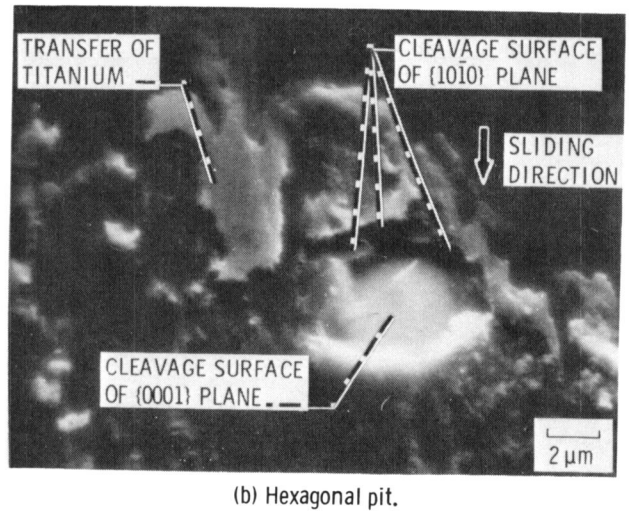


(b) Unoccupied antibonding.

Figure 12. - Fe(d) - O(p) molecular-orbital wave-function contour maps for an iron atom supported on sapphire, plotted in the plane of the iron atom and two surface oxygen atoms. The solid and dashed contours represent the positive and negative phases of the wave function



(a) Hexagonal cracking.



(b) Hexagonal pit.

Figure 13. - Scanning electron photomicrographs of wear tracks on the {0001} surface of single-crystal SiC in contact with rhodium and titanium as a result of ten passes of a rider in vacuum. Sliding direction, $<10\bar{1}0>$; sliding velocity, 3 mm/min^{-1}; load, 0.3 N; room temperature; pressure, 30 nPa; metal pin rider, 0.79 mm radius.

SOME DESIGN CONSIDERATIONS FOR CERAMIC COMPONENTS IN HEAT ENGINE APPLICATIONS

John P. Gyekenyesi
NASA Lewis Research Center
Cleveland, Ohio 44135

This presentation reviews the design methodology for brittle material structures which is being developed and used at the Lewis Research Center for sizing ceramic components in heat engine applications. Theoretical aspects of designing with structural ceramics are discussed, and a general purpose reliability program for predicting fast fracture response due to volume distributed flaws is described. Statistical treatment of brittle behavior, based on the Weibull model, is reviewed and its advantages, as well as drawbacks, are listed. A mechanistic statistical fracture theory, proposed by Batdorf to overcome the Weibull model limitations and based on Griffith fracture mechanics, is summarized. Failure probability predictions are made for rotating annular Si_3N_4 disks using various fracture models, and the results are compared to actual failure data. The application of these design methods to Government funded ceramics engine demonstration programs is surveyed. The uncertainty in observed component performance emphasizes the need for proof testing and improved NDE technology to guarantee adequate structural integrity.

POSSIBLE APPROACHES TO CERAMIC DESIGN

A. PROTOTYPE TESTING
- NO STRESS ANALYSIS REQUIRED
- POLYAXIAL FRACTURE STRESS THEORY NOT NEEDED
- EVERY DESIGN IS UNIQUE
- EXPENSIVE

B. SCALE MODEL EVALUATION
- VOLUME EFFECT MUST BE INCLUDED
- NO MECHANICAL STRESS ANALYSIS NEEDED
- POLYAXIAL FRACTURE STRESS THEORY NOT NEEDED
- THERMAL STRESS PROBLEM CANNOT BE SCALED
- EVERY DESIGN IS UNIQUE
- LESS EXPENSIVE

C. USE OF TEST SPECIMEN TESTING
- VOLUME EFFECT MUST BE INCLUDED
- FULL THERMOMECHANICAL ANALYSIS REQUIRED
- COMBINED FRACTURE STRESS THEORY NEEDED
- CAN BE APPLIED TO ALL DESIGNS
- INEXPENSIVE

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POTENTIAL FAILURE MODES IN HEAT ENGINES

A. TIME INDEPENDENT FAILURE MODES
- FAST FRACTURE (TENSION-COMPRESSION)
- BUCKLING

B. TIME DEPENDENT FAILURE MODES
- STATIC FATIGUE
- DYNAMIC FATIGUE
- CREEP CRACK GROWTH
- STRESS CORROSION AND OXIDATION
- IMPACT AND DYNAMIC LOADING

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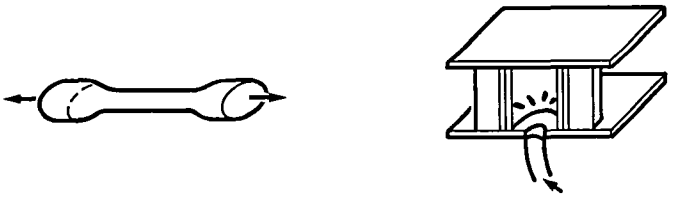
SCHEMATICS OF STRENGTH TESTS



UNIAXIAL TENSILE STRENGTH

HYDROSTATIC TENSILE

3-POINT BENDING

4-POINT BENDING

UNIAXIAL COMPRESSIVE

DIAMETRAL COMPRESSION

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BRITTLE MATERIAL DESIGN METHOD

MATERIAL BRITTLENESS AND PRESENCE OF MICROCRACKS REQUIRES

- ALLOWANCE FOR STRENGTH DISPERSION - PROBABILISTIC APPROACH
- CONSIDERATION OF MATERIAL VOLUME UNDER STRESS (COMBINATION OF STRESS AND VOLUME DETERMINE INTEGRITY)
- REFINED THERMAL AND STRESS ANALYSIS - FIELD SOLUTIONS (EXAMINATION OF CRITICAL POINT IS NOT ADEQUATE)

DESIGN PRACTICE

- FAILURE MODE IS FRACTURE DUE TO CRACK PROPAGATION
- PROOF TESTING AND/OR NDE REQUIRED TO TRUNCATE STRENGTH DISTRIBUTION - ESTABLISH ALLOWABLE STRESS
- NO DESIGN CODES AND ONLY LIMITED EXPERIENCE AVAILABLE

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FRACTURE THEORIES

I. GRIFFITH (1920 AND 1924)

- CRACK SHAPE, SIZE, ORIENTATION SPECIFIED
- IGNORES VOLUME EFFECT
- USES MECHANISTIC FRACTURE CRITERION
- APPROACH IS DETERMINISTIC (BASIS FOR LEFM)

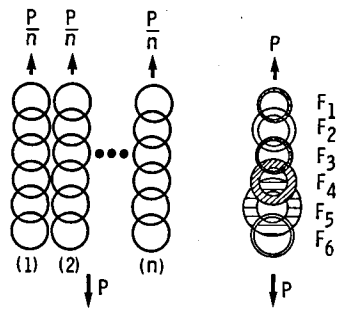
II. WEIBULL (1939)

- CRACK SHAPE, SIZE, ORIENTATION NOT SPECIFIED
- INCLUDES ALLOWANCE FOR STRENGTH DISPERSION
- EXPLAINS VOLUME EFFECT
- USES EMPIRICAL FRACTURE CRITERION
- APPROACH IS PROBABILISTIC

STATISTICAL TREATMENTS

WEAKEST LINK THEORY FOR TENSILE LOADING

- MATERIAL CONTAINS N FLAWS OR LINKS
- EACH FLAW OR LINK HAS A σ_{cr}
- UPON SINGLE LINK FAILURE, TWO REDISTRIBUTION MECHANISMS ARE POSSIBLE



SERIES-PARALLEL MODEL SERIES MODEL

- STRUCTURAL CERAMICS ARE ASSUMED TO FOLLOW THE SERIES MODEL
- FAILURE OF SINGLE LINK IMPLIES COMPONENT FAILURE, NO CRACK ARREST MECHANISM EXISTS

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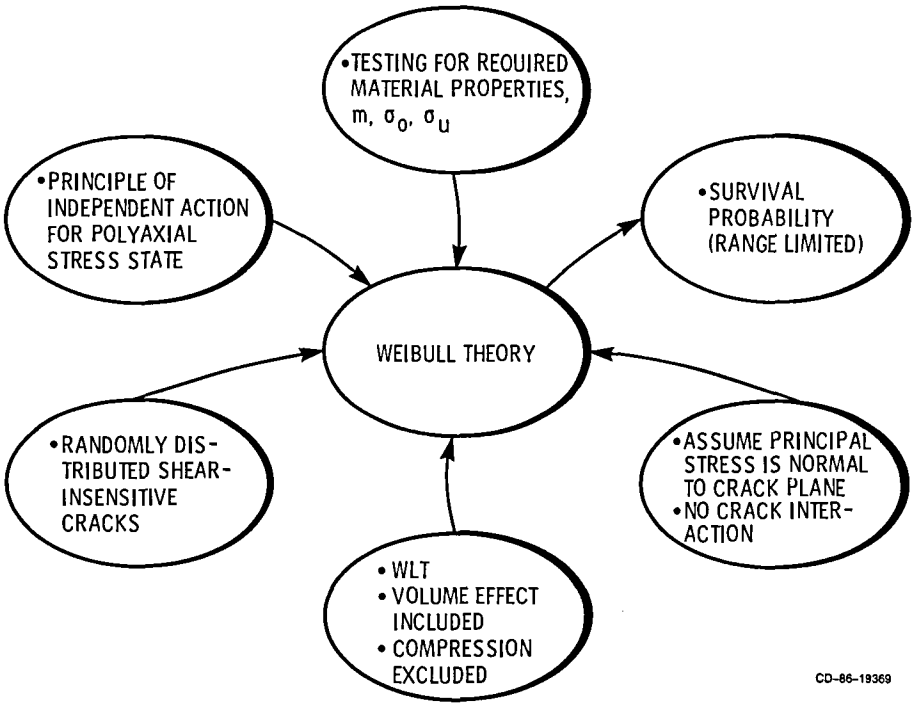
ELEMENTS OF WEIBULL'S THEORY (1)



WEIBULL THEORY (2) (CONTINUED)

SURVIVAL PROBABILITY	EQUATION
IN UNIAXIAL TENSION	$P_S(\sigma) = P_S^V(\sigma) \cdot P_S^A(\sigma)$
DUE TO VOLUME CRACKS	$P_S^V(\sigma) = \exp\left[-\int_V \left(\frac{\sigma - \sigma_u^V}{\sigma_0^V}\right)^{m_V} dv\right]$
DUE TO SURFACE CRACKS	$P_S^A(\sigma) = \exp\left[-\int_A \left(\frac{\sigma - \sigma_u^A}{\sigma_0^A}\right)^{m_A} dA\right]$
IN POLYAXIAL TENSION	$P_S(\sigma_1,\sigma_2,\sigma_3) = P_S(\sigma_1) \cdot P_S(\sigma_2) \cdot P_S(\sigma_3)$

WHERE σ = APPLIED STRESS AND $\sigma_1,\sigma_2,\sigma_3$ = PRINCIPAL STRESSES.

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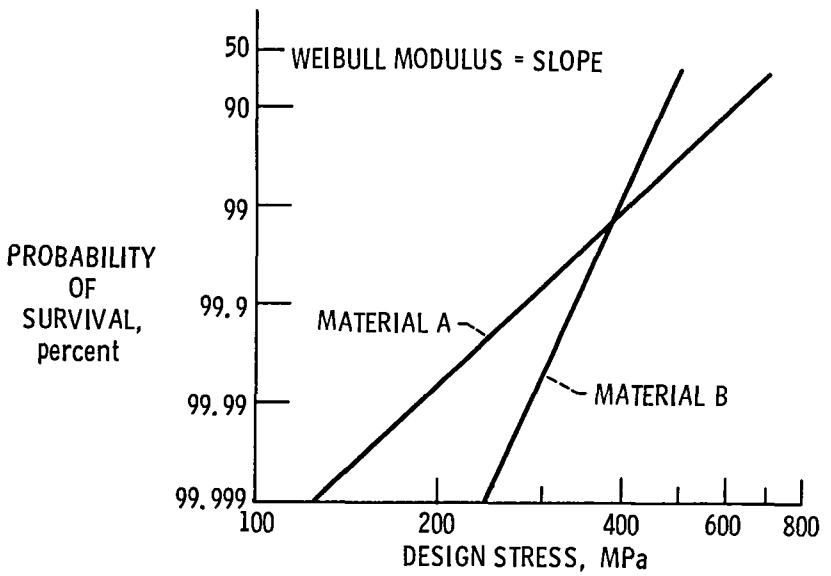
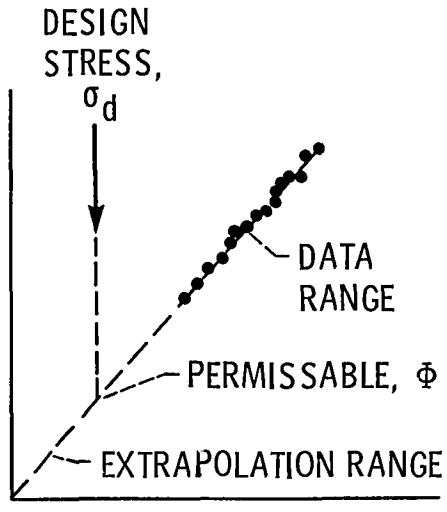
HYPOTHETICAL EXAMPLE OF IMPORTANCE OF HIGH WEIBULL MODULUS FOR STRUCTURAL CERAMICS



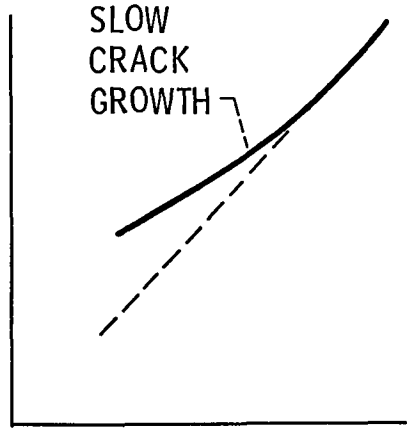
ADVANTAGES OF PROBABILISTIC DESIGN

- PERMITS EFFICIENT MATERIAL UTILIZATION
- INCLUDES TRADE-OFF BETWEEN HIGH STRENGTH AND LOW SCATTER
- ACCOUNTS FOR MATERIAL STRENGTH DISPERSION
- INCLUDES COMPONENT SIZE EFFECT

LIMITATIONS OF THE DIRECT STATISTICAL APPROACH

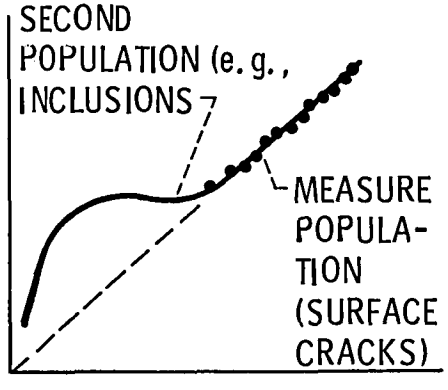


BASIC DATA

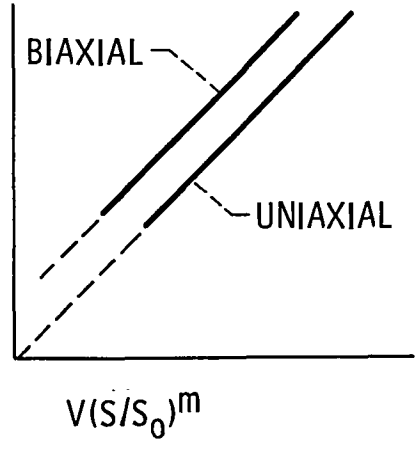


EFFECTS OF SLOW CRACK GROWTH

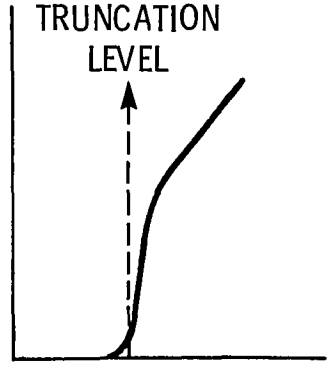
$-\ln(1 - \Phi)$



UNDETECTED FLAW POPULATIONS



STRESS STATE EFFECTS



TRUNCATION PROCEDURES

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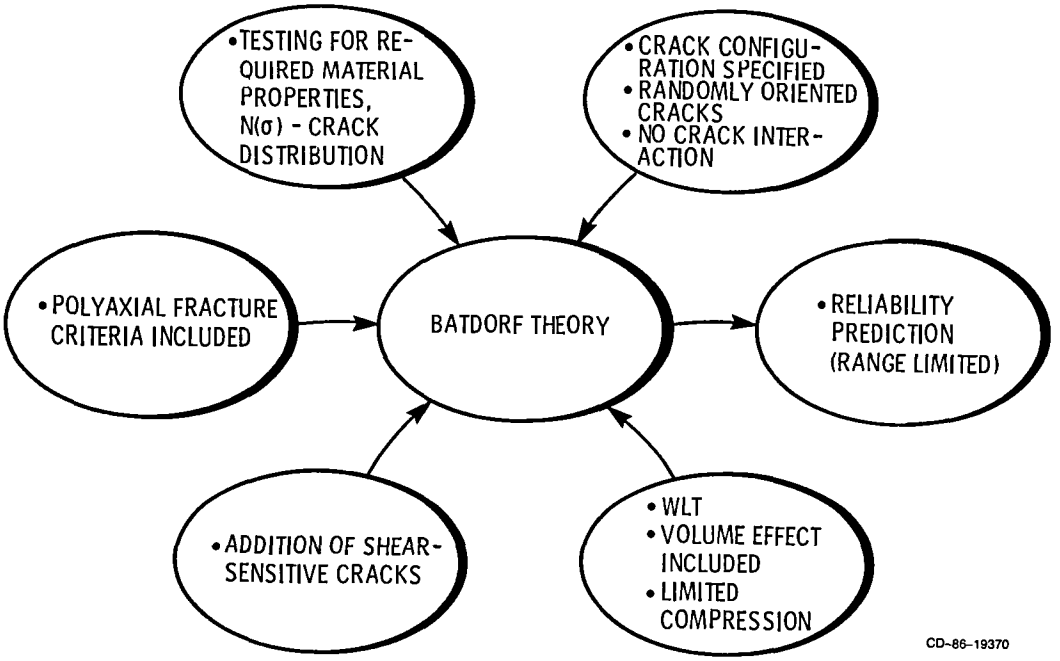
ELEMENTS OF BATDORF'S THEORY (1)



BATDORF THEORY (2) (CONTINUED)

$$P_s(\Sigma) = P_s^V \cdot P_s^A$$

$$P_s^V = \exp\left(-\iint_V \int_0^{\sigma_1} \frac{\Omega}{4\pi} \frac{dN_1}{d\sigma_{cr}}\, d\sigma_{cr} dv\right)$$

$$P_s^A = \exp\left(-\iint_A \int_0^{\sigma_1} \frac{\omega}{\pi} \frac{dN_2}{d\sigma_{cr}}\, d\sigma_{cr} dA\right)$$

$$N_1 = K_1 \sigma_{cr}^{m_1}$$

$$N_2 = K_2 \sigma_{cr}^{m_2}$$

$$\omega = f_1(\sigma_{cr}, \sigma_1, \sigma_2)$$

$$\Omega = f_2(\sigma_{cr}, \sigma_1, \sigma_2, \sigma_3, \alpha)$$

$\sigma_e = f_3(\sigma_n, \tau)$, f_3 DEPENDS UPON THE FRACTURE CRITERION SELECTED

$$\sigma_n = f_4(\sigma_1, \sigma_2, \sigma_3, \alpha, \beta)$$

$$\tau = f_5(\sigma_1, \sigma_2, \sigma_3, \alpha, \beta)$$

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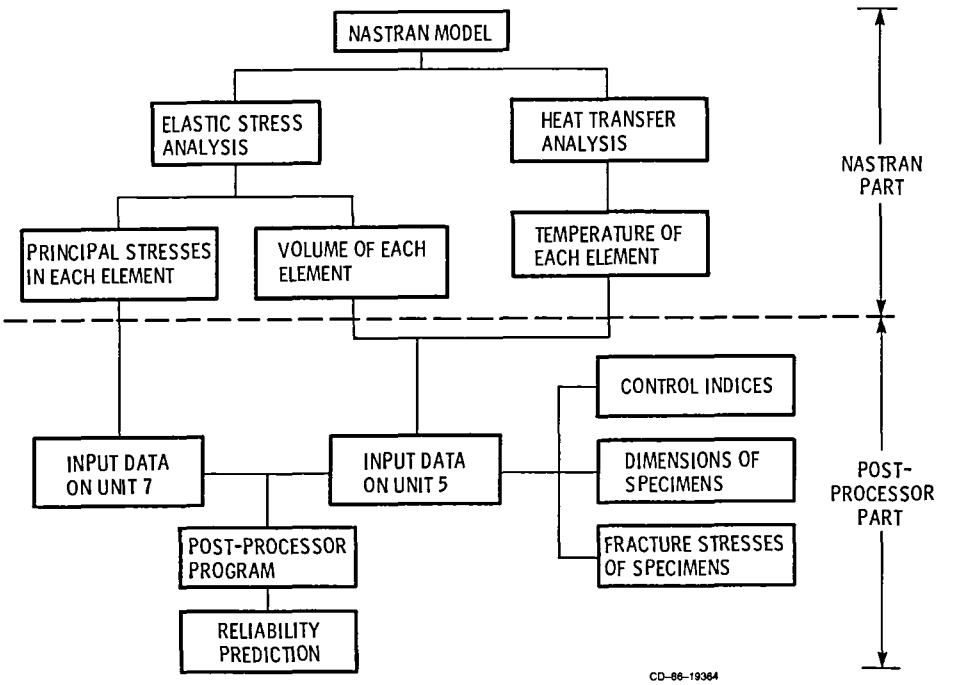
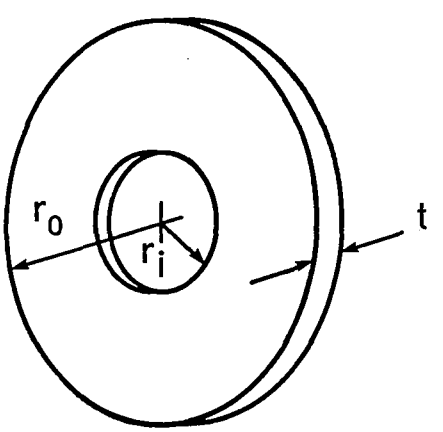
FLOW CHART FOR RELIABILITY PREDICTION
(VOLUME FLAWS ONLY)



EXAMPLE 1 - ROTATING ANNULAR DISK



DATA:

NC - 132 HOT PRESSED Si_3N_4

$m = 7.65$

$\sigma_0 = 74.82 \text{ MPa m}^{.3922}$

$\overline{k}_B = 16.30$

$r_i = 6.35$ mm (.25 in)

$r_o = 41.275$ mm (1.625 in)

$t = 3.80$ mm (.15 in)

RPM RANGE - 70K TO 114K

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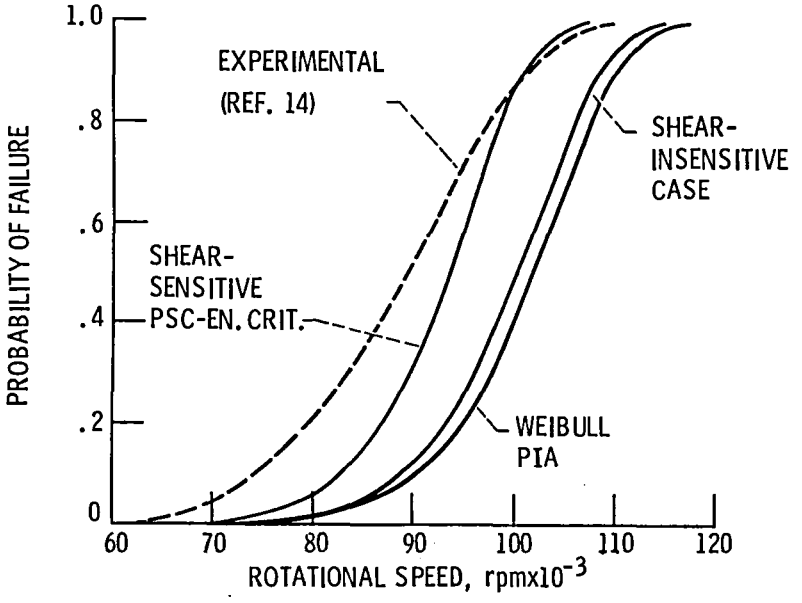

Fig. 7 Example 1 probability of failure vs disk rotational speed for various fracture models (SCARE2 data).

APPLICATION TO CERAMICS

- INITIALLY ONLY WEIBULL THEORY WAS USED (INCLUDES CATE, AGT, AND DARPA PROGRAMS)
- LIMITED SUCCESS AND ACCURACY OBTAINED
- BATDORF BRIDGES GAP BETWEEN FRACTURE THEORIES IN 1974 (GRAPHITE NOSE CONES)
- UNIVERSITY OF WASHINGTON (UW) APPLIES BATDORF'S THEORY TO CERAMICS (NASA GRANT)
- LeRC CORRECTS UW PUBLICATIONS AND DEVELOPS GENERAL PURPOSE DESIGN PROGRAM - SCARE
- SCARE INCLUDES WEIBULL AND BATDORF THEORIES
- SCARE RELEASED TO GM, FORD, TRW, BOEING, GE, AND NASA AND ARMY FOR INITIAL EVALUATION

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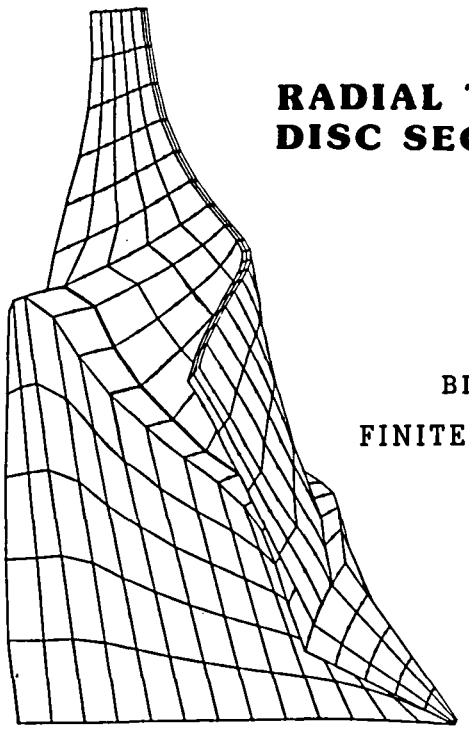

RADIAL TURBINE BLADE DISC SECTOR ANALYSIS

CERAMIC

BLADE - DISC

FINITE ELEMENT MODEL

CONCLUSIONS

1. PROBABILISTIC DESIGN APPROACH AND WLT MUST BE USED FOR CERAMICS
2. FRACTURE MECHANICS MUST BE APPLIED TO IMPROVE MODELING OF:
   - MULTI-AXIALITY EFFECT
   - DELAYED FAILURE
3. PROOF-TESTING AND/OR NDE SHOULD BE USED TO AVOID DATA EXTRAPOLATION
4. MULTIPLE FLAW DISTRIBUTIONS SHOULD BE INCLUDED IN THE ANALYSIS
5. IMPROVED FRACTURE TOUGHNESS AND MATERIAL PROCESSING ARE NEEDED TO INCREASE CERAMIC STRENGTH

CD-86-19361

NONDESTRUCTIVE EVALUATION OF STRUCTURAL CERAMICS*

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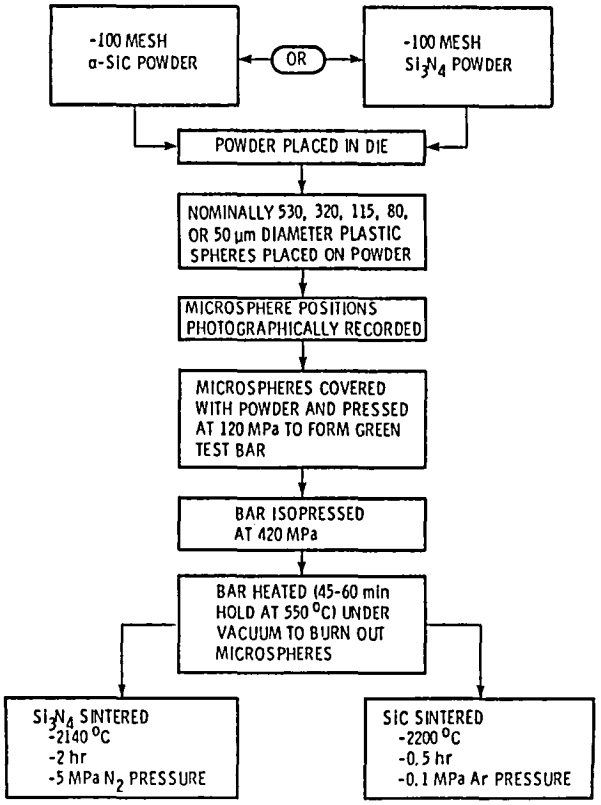
A review is presented on research for nondestructive evaluation (NDE) of structural ceramics for heat engine applications. Microfocus radiography and scanning laser acoustic microscopy are the NDE techniques highlighted in this review. The techniques were applied to research samples of sintered silicon nitride and silicon carbide in the form of modulus-of-rupture (MOR) bars. The strengths and limitations of the aforementioned techniques are given in terms of probability of detection for voids in green and sintered MOR bars. Voids for this purpose were introduced by seeding green ceramic bars and characterizing each void in terms of its size, shape, location, and nature before and after sintering. The effects of material density, microstructure, surface finish, thickness, void depth, and size characteristics on detectability are summarized. The review presented here is based on the work of Stanley Klima, Don Roth, George Baaklini, William Sanders, and James Kiser of Lewis Research Center, Cleveland, Ohio.

FABRICATION OF MODULUS-OF-RUPTURE (MOR) BARS CONTAINING SEEDED INTERNAL VOIDS



EXPERIMENTAL/ANALYTICAL

- SPECIALLY PREPARED MODULUS-OF-RUPTURE TYPE BARS WERE SYSTEMATICALLY SEEDED WITH CRITICAL SIZE VOIDS
- VOIDS RESULTED AFTER THE STYRENE DIVINYL BENZENE MICROSPHERES WERE DECOMPOSED IN THE GREEN CERAMICS AT 550° C
- POD STATISTICS WERE DETERMINED USING THE CUMULATIVE PROBABILITY FORMULA

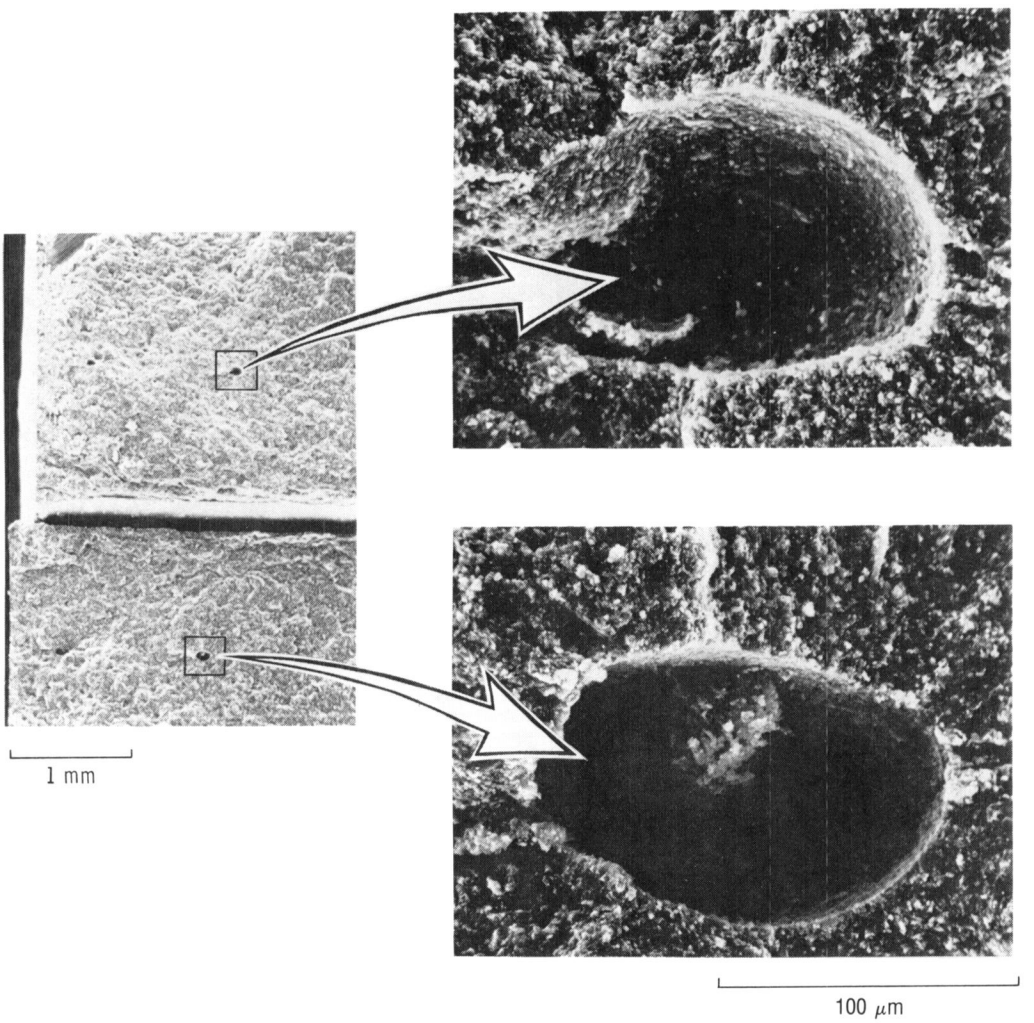
$$1 - G = \sum_{X=S}^{N} \frac{N!}{X!\,(N-X)!}\, P_L^{\,X}\,(1-P_L)^{N-X}$$

WHERE P_L IS THE LOWER-BOUND PROBABILITY OF DETECTION, G IS THE CONFIDENCE LEVEL, N IS THE NUMBER OF VOIDS SEEDED, AND S IS THE NUMBER OF VOID DETECTED

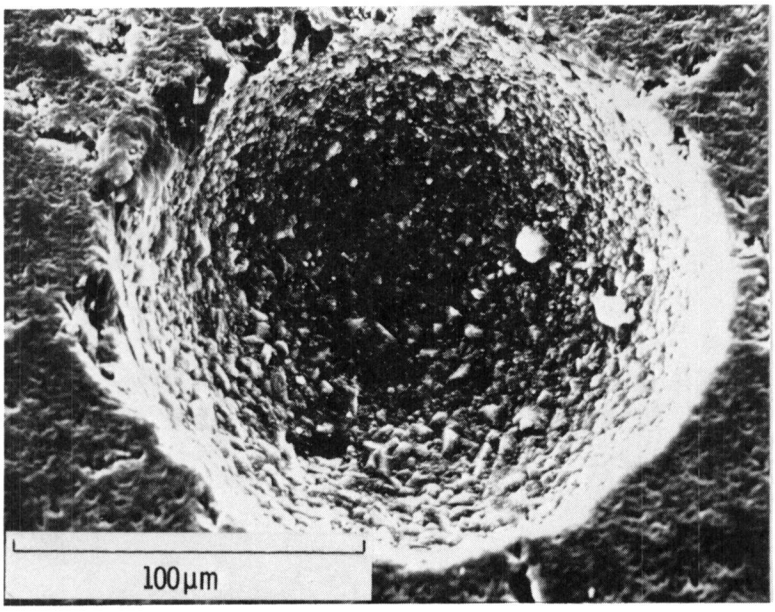
DIMENSIONAL CHARACTERISTICS OF RESULTING INTERNAL VOIDS IN SINTERED MATERIALS

MATERIALS	SPECIMEN THICKNESS RANGE,	SPHERE diam, μm	NUMBER OF SPHERES SEEDED	RESULTING VOID DIMENSION VOID DEPTH, μm		VOID DIAMETER, μm	
				MEAN	STANDARD DEVIATION	MEAN	STANDARD DEVIATION
Si_3N_4	2-7	80	69	20	4	25	6
		115	39	37	5	68	5
		200	31	133	17	139	8
		321	28	233	16	267	18
		528	21	307	14	386	15
SiC	2-7	50	50	32	3	58	3
		80	47	59	6	100	8
		115	68	77	10	131	8
		200	19	165	29	194	11
		321	39	297	19	307	15
		528	43	477	47	505	28

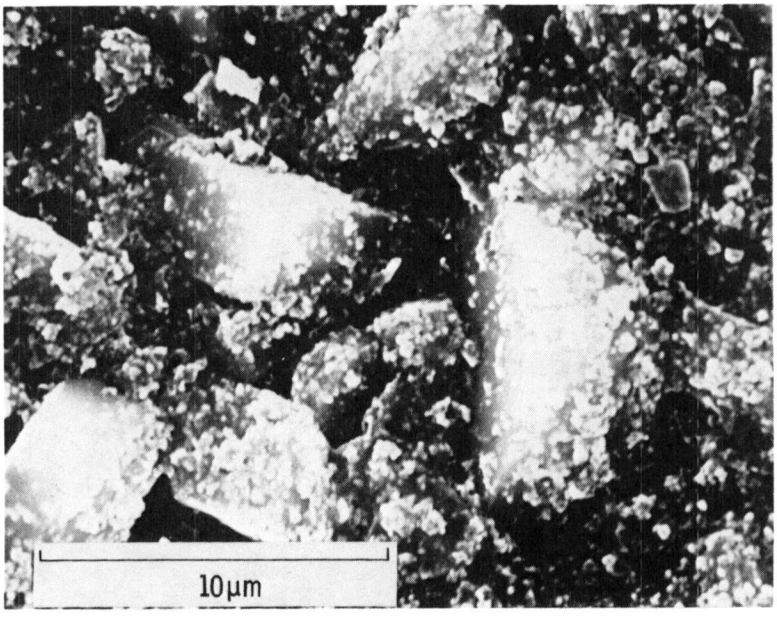
SCANNING ELECTRON FRACTOGRAPHS SHOWING TYPICAL INTERNAL VOIDS IN GREEN SiC BARS



SCANNING ELECTRON MICROGRAPHS OF A TYPICAL VOID IN SINTERED SiC BARS

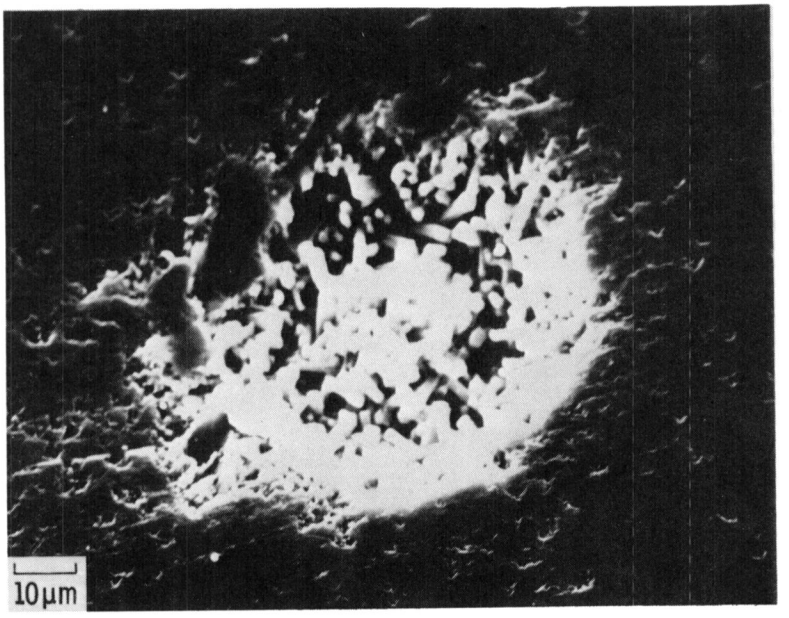


AS EXPOSED TO SURFACE

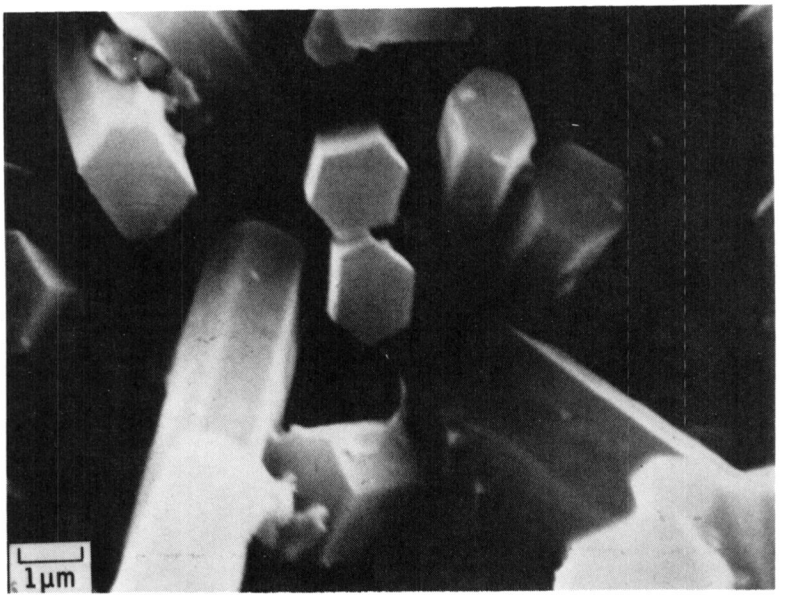


TEXTURE OF THE CAVITY-WALL-SURFACE

SCANNING ELECTRON MICROGRAPHS OF TYPE A INTERNAL VOIDS IN SINTERED Si_3N_4

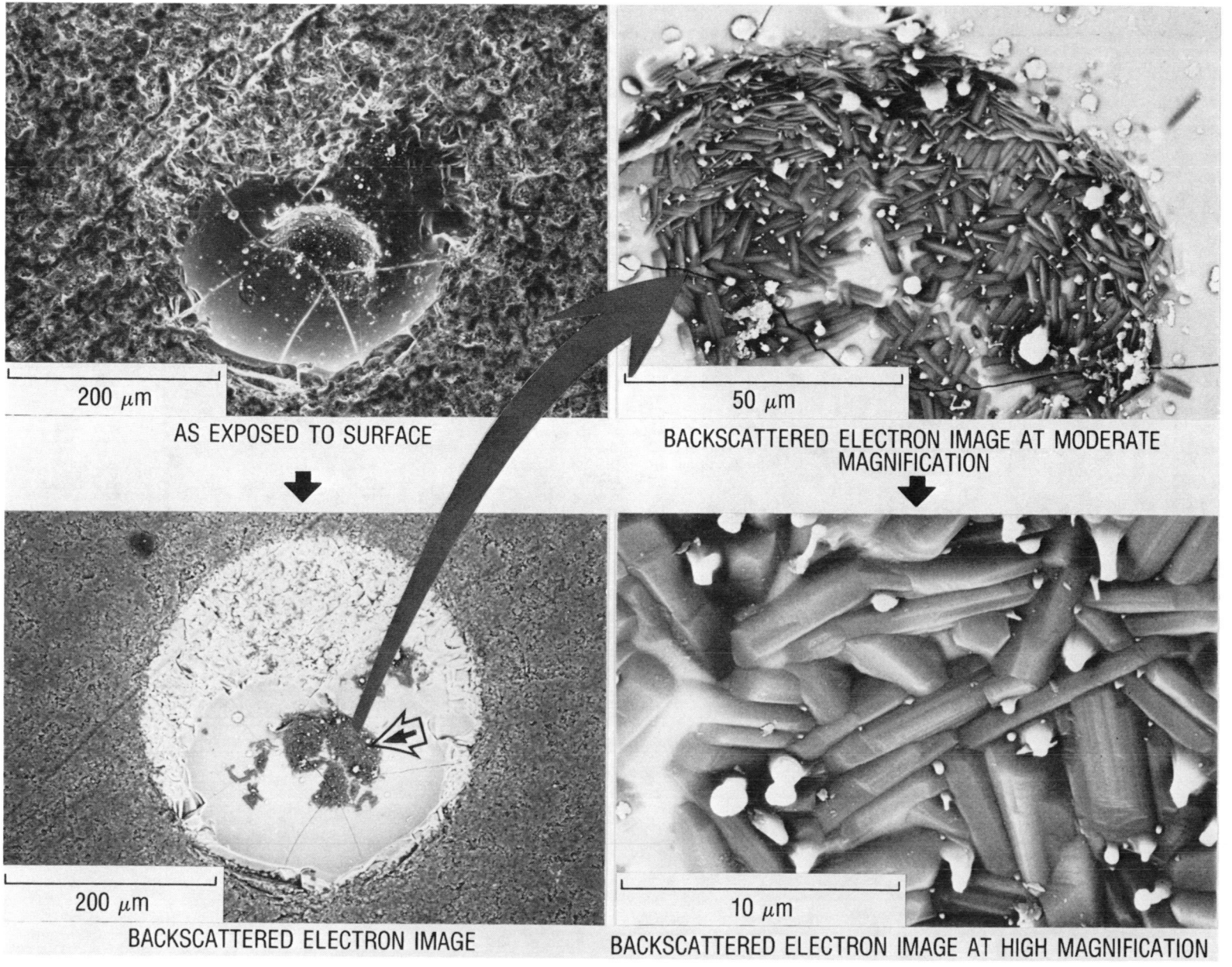


AS EXPOSED TO SURFACE

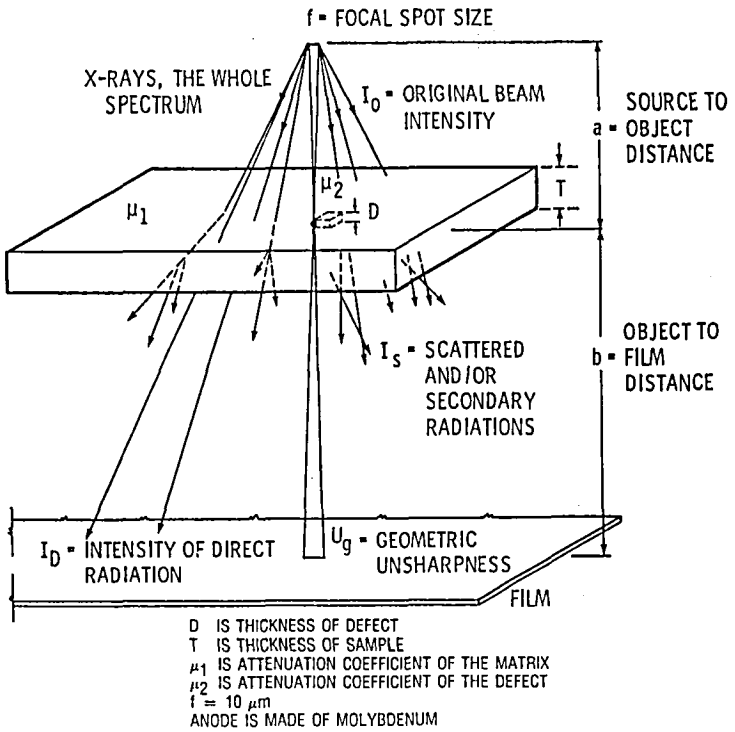


CLUSTERS OF GRAINS PROJECTING FROM THE CAVITY WALLS

SCANNING ELECTRON MICROGRAPHS OF TYPE B INTERNAL VOIDS IN SINTERED Si_3N_4



A SCHEMATIC CONFIGURATION OF MICROFOCUS PROJECTION RADIOGRAPHY



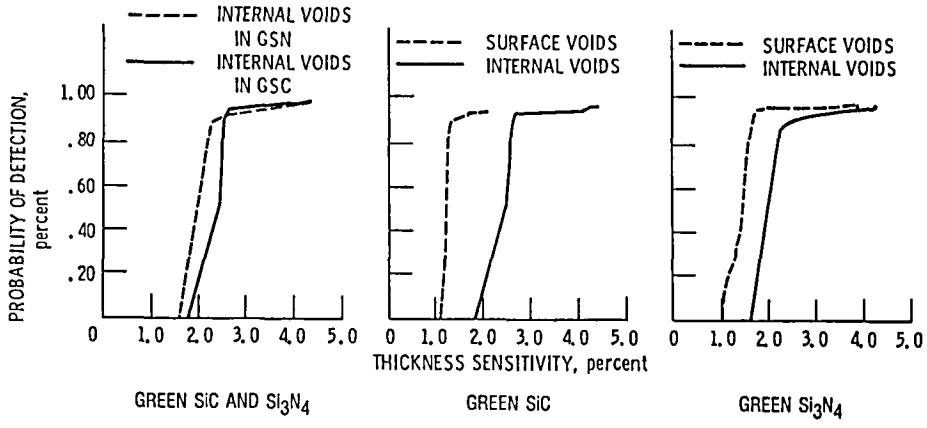
MICROFOCUS RADIOGRAPHY

SUMMARY OF POD STATISTICS FOR INTERNAL AND SURFACE VOIDS IN GREEN AND SINTERED SiC AND Si_3N_4

MATERIALS		OPTIMUM SENSITIVITY AT 90/95 POD/CL• (GIVEN AS PERCENT OF SAMPLE THICKNESS)	
		INTERNAL VOIDS	SURFACE VOIDS
SiC	GREEN	2.6	1.4
	SINTERED	1.5	1.7
Si_3N_4	GREEN	2.4	1.5
	SINTERED	0.6	1.5

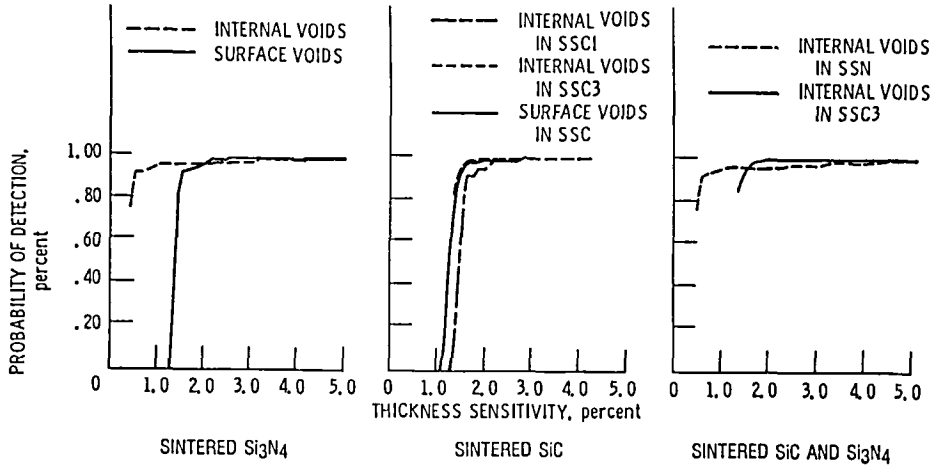
- 90/95 POD/CL (PROBABILITY OF DETECTION/CONFIDENCE LEVEL) MEANS THAT THERE IS A 5% PROBABILITY THAT THE 90% IS AN OVERESTIMATE OF THE PROBABILITY OF DETECTION

LOWER BOUND PROBABILITY OF DETECTION OF SURFACE AND INTERNAL VOIDS IN GREEN ISOPRESSED SiC (GSC) AND Si_3N_4 (GSN) BARS



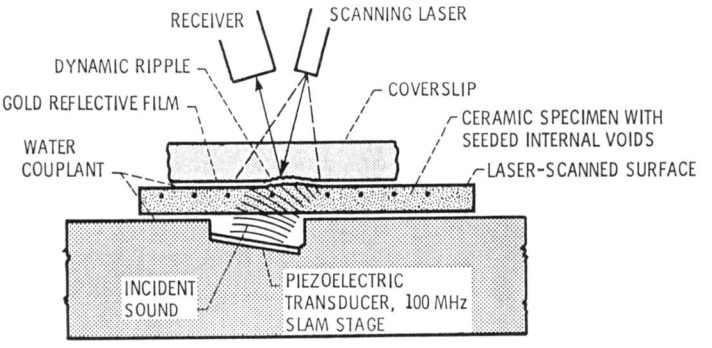
- POD CURVES WERE CALCULATED AT 95 PERCENT CONFIDENCE LEVEL
- THICKNESS SENSITIVITY % =100 (VOID DIMENSION IN X-RAY BEAM DIRECTION)/ (THICKNESS OF SPECIMEN IN SAME DIRECTION)

LOWER BOUND PROBABILITY OF DETECTION OF SURFACE AND INTERNAL VOIDS IN SINTERED SiC (SSC) AND Si_3N_4 (SSN) BARS



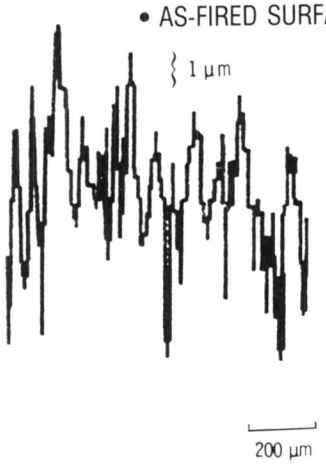
- POD CURVES WERE CALCULATED AT 95 PERCENT CONFIDENCE LEVEL
- THICKNESS SENSITIVITY % = 100 (VOID DIMENSION IN X-RAY BEAM DIRECTION)/(THICKNESS OF SPECIMEN IN SAME DIRECTION

SCHEMATIC ILLUSTRATION OF THE SCANNING LASER ACOUSTIC MICROSCOPE

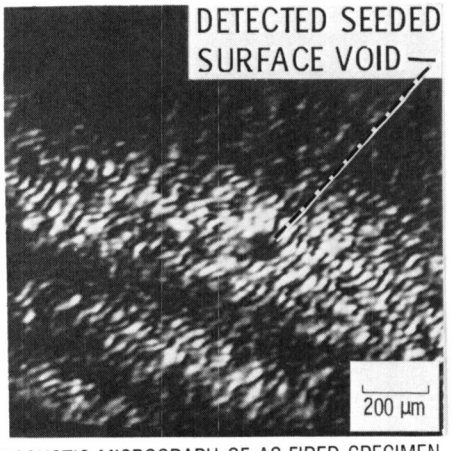


EFFECT OF SPECIMEN SURFACE CONDITION ON SLAM IMAGE CLARITY

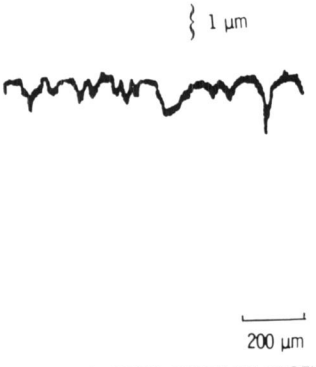
- AS-FIRED SURFACE PRODUCES A HIGHER BACKGROUND NOISE LEVEL



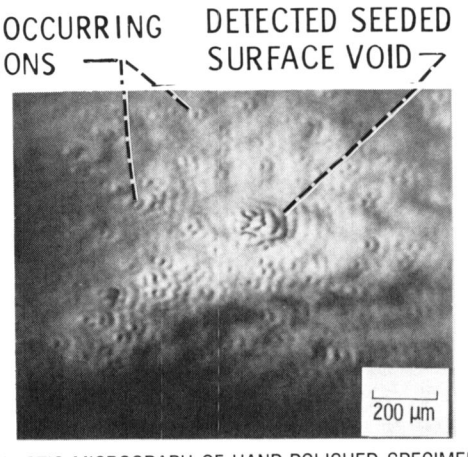
AS-FIRED SURFACE PROFILE.



ACOUSTIC MICROGRAPH OF AS-FIRED SPECIMEN.

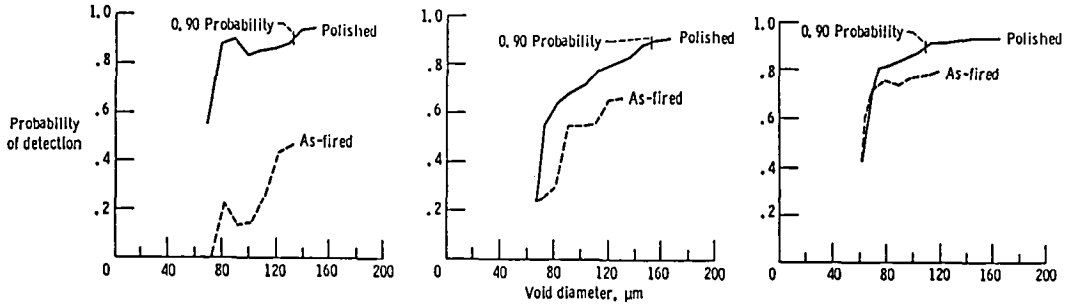


HAND-POLISHED SURFACE PROFILE.



ACOUSTIC MICROGRAPH OF HAND-POLISHED SPECIMEN.

EFFECT OF SURFACE FINISH AND SPECIMEN THICKNESS ON DETECTION OF VOIDS IN SSN



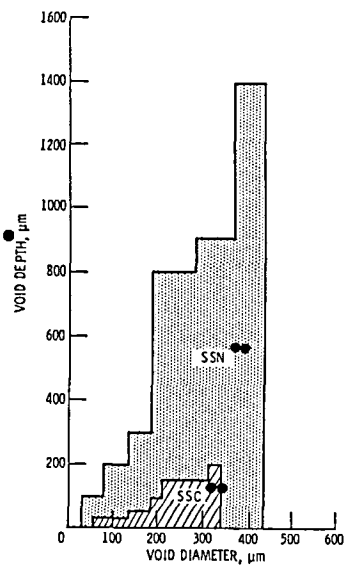
(a) SPECIMEN THICKNESS, APPROXIMATELY 4 mm.

(b) SPECIMEN THICKNESS, APPROXIMATELY 3 mm.

(c) SPECIMEN THICKNESS, APPROXIMATELY 2 mm.

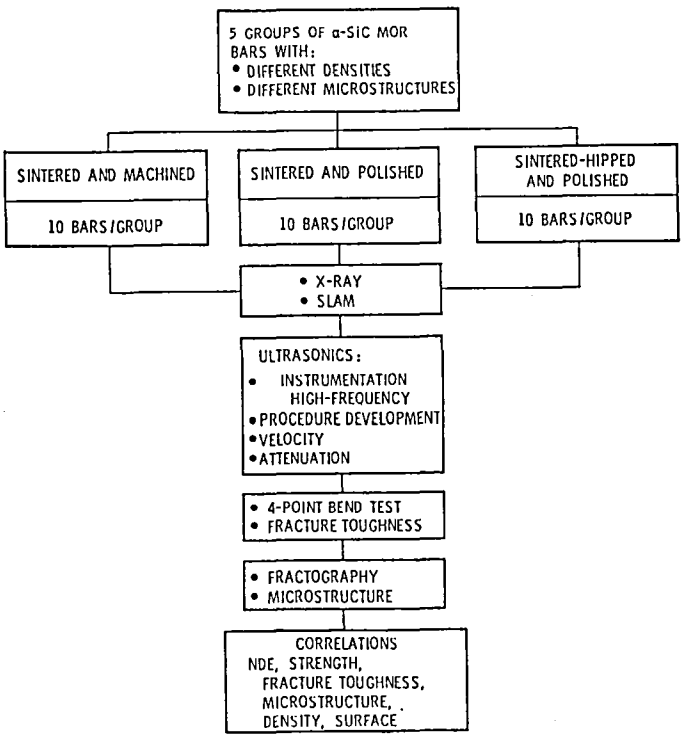
EFFECT OF VOID DIAMETER, VOID DEPTH, AND MATRIX MATERIAL ON PROBABILITY OF DETECTION BY SLAM

90% PROBABILITY OF DETECTION AT 95% CONFIDENCE LIMIT



- DEPTH BELOW WHICH A VOID WITH A SPECIFIED DIAMETER CANNOT BE DETECTED AT POD/CL = 90/95
- •• DETECTABILITY OF SMALLER, DEEPER VOIDS IN SSN MAY BE ATTRIBUTABLE TO FINER GRAINS AND GREATER DENSITY (SSN AT > 99% VS SSC AT ~97% THEORETICAL DENSITY)

NDE FOR CHARACTERIZING CERAMIC MICROSTRUCTURES



ASSESSMENT OF FRACTURE ORIGINS FOR NASA 6Y SINTERED Si_3N_4

			SUB-SURFACE PORE	SURFACE PORE	SEAM	SUB-SURFACE AGGLOMERATE	COLUMNAR GRAIN	SURFACE DEFECT	METALLIC INCLUSION
R.T. FLEXURE TEST	TOTAL FRACTURE ORIGINS IDENTIFIED	192[a]	56	44	28	25	17	13	9
	PERCENT OF TOTAL	100	29	23	14	13	9	7	5
1200 °C FLEXURE TEST	TOTAL FRACTURE ORIGINS IDENTIFIED	90[a]	23	19	9	7	14	0	18
	PERCENT OF TOTAL	100	26	21	10	8	15	0	20
1370 °C FLEXURE TEST	TOTAL FRACTURE ORIGINS IDENTIFIED	127[a]	30	15	25	3	32	0	22
	PERCENT OF TOTAL	100	24	12	20	2	25	0	17

[a]NUMBER EXCLUDES 111, 47, AND 41 BARS FOR R.T., 1200 °C, AND 1370 °C, RESPECTIVELY, WHERE FLAW REGION OR FLAW TYPE COULD NOT BE DETERMINED.

SUMMARY

SCANNING LASER ACOUSTIC MICROSCOPY

VOID DETECTABILITY WAS AFFECTED BY MATERIAL, MICROSTRUCTURE, SURFACE FINISH, SPECIMEN THICKNESS, VOID DEPTH, AND VOID SIZE.

- VOIDS WERE MORE EASILY DETECTED IN SINTERED SILICON NITRIDE (SSN) THAN IN SINTERED SILICON CARBIDE (SSC). SSN GRAIN SIZE WAS AN ORDER OF MAGNITUDE SMALLER THAN IN SSC.
- VOID DETECTABILITY WAS SIGNIFICANTLY IMPROVED BY SURFACE GRINDING. IN SPECIMENS WITH AS-FIRED SURFACES, 0.90/0.95 POD/CL WAS NOT ACHIEVED FOR ANY VOID SIZE UP TO 160 μm.
- LITTLE OR NO THICKNESS EFFECT ON DETECTABILITY WAS OBSERVED IN SPECIMENS WITH GROUND SURFACES. IN SPECIMENS WITH AS-FIRED SURFACES, DETECTABILITY IMPROVED WITH DECREASING THICKNESS.

MICROFOCUS X-RAY RADIOGRAPHY

DETECTABILITY OF VOIDS WAS AFFECTED BY PHOTON ENERGY LEVEL, MATERIAL COMPOSITION IN THE VICINITY OF THE VOID, DENSITY VARIATIONS, SAMPLE THICKNESS AND VOID SIZE.

- LOW PHOTON ENERGY LEVELS ($\leq$20 KeV) PRODUCED BETTER RADIOGRAPHIC FILM CONTRAST AND HENCE BETTER VOID DETECTABILITY THAN HIGHER ENERGY LEVELS.
- YITTRIUM MIGRATING TO THE WALLS OF SEEDED VOIDS AIDED DETECTION OF SOME BUT NOT ALL VOIDS IN SSN. YITTRIA SINTERING AID WAS THE SOURCE.
- DETECTABILITY OF VOIDS DID NOT APPEAR TO BE ADVERSELY AFFECTED BY AS-FIRED SURFACES RELATIVE TO DIAMOND GROUND SURFACES.
- THE THRESHOLD LEVEL OF DETECTION OF VOIDS WAS 1.5 PERCENT OF SPECIMEN THICKNESS OR 50 μm, WHICHEVER IS GREATER, WHEN THE 0.90/0.95 POD/CL CRITERIA WAS APPLIED.

FRACTURE MECHANICS

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The application of fracture mechanics to the design of ceramic structures will require the precise measurement of crack growth and fracture resistance of these materials over their entire range of anticipated service temperatures and standardized test methods for making such measurements. The development of a standard test for measuring the plane strain fracture toughness is the initial objective of our ceramics fracture mechanics program.

Current fracture tests make use of a variety of specimen types (single-edge-notched bend, double torsion, double cantilever bend, and surface flawed specimens) having either blunt notches produced by saw cutting, or cracks produced by wedge loading, indenting, or local thermal shock. Specimens with blunt notches can overestimate the fracture toughness. Precracked specimens are difficult to prepare in a reproducible manner, and the initial crack front often cannot be seen on the fracture surface after testing, which makes it impossible to measure the initial crack length. These difficulties can be circumvented by using a specimen containing a chevron notch in which a crack originates at the tip of the triangular ligament during the early stage of specimen loading. Specimens with a chevron notch were first used by Nakayama in fracture studies (ref. 1). Later they were used by Tattersall and Tappin for fracture surface energy measurements (ref. 2) and more recently, by Barker for plane strain fracture toughness measurements (ref. 3). The essential features of the chevron-notch specimen are that (1) a sharp natural crack is produced during the early stage of loading (no precracking is required) and (2) the load passes through a maximum at a constant material-independent crack length-to-width ratio for a specific specimen geometry (no post-test crack length measurement is required). For materials with flat crack growth resistance curves, the plane strain fracture toughness is proportional to the maximum test load and a function of the specimen geometry and elastic compliance.

Stress intensity factor coefficients have been determined for three varieties of chevron-notch specimens, and fracture toughness measurements have been made on silicon nitride, silicon carbide, and aluminum oxide to assess the performance of each specimen variety. It has been determined that silicon nitride and silicon carbide have flat crack growth resistance curves, but aluminum oxide does not. Additionally, batch-to-batch differences have been noticed for the aluminum oxide. Experiments are continuing to explain the rising crack growth resistance and batch-to-batch variations for the aluminum oxide.

REFERENCES

1. Nakayama, J.: Direct Measurement of Fracture Energies of Brittle Heterogeneous Materials. J. Am. Ceram. Soc., vol. 48, no. 11, 1965, pp. 583-587.

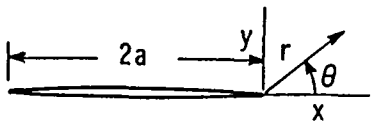
2. Tattersall, H.G.; and Tappin, G.: The Work of Fracture and Its Measurement in Metals, Ceramics and other Materials. J. Mater. Sci., vol. 1, no. 3, 1966, pp. 296-301.

3. Barker, L.M.: A Simplified Method for Measuring Plane Strain Fracture Toughness. Eng. Fracture Mech., vol. 9, no. 2, 1977, pp. 361-369.

PLANE STRAIN ELASTIC STRESS FIELD IN VICINITY OF CRACK TIP

$$\sigma_x = \frac{K_I}{(2\pi r)^{1/2}} \cos\frac{\theta}{2}\left(1 - \sin\frac{\theta}{2}\sin\frac{3\theta}{2}\right) + \ldots$$

$$\sigma_y = \frac{K_I}{(2\pi r)^{1/2}} \cos\frac{\theta}{2}\left(1 + \sin\frac{\theta}{2}\sin\frac{3\theta}{2}\right) + \ldots$$



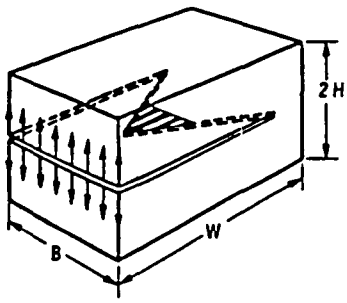
$$\tau_{xy} = \frac{K_I}{(2\pi r)^{1/2}} \sin\frac{\theta}{2}\cos\frac{\theta}{2}\cos\frac{3\theta}{2} + \ldots$$

$$\sigma_z = \nu(\sigma_x + \sigma_y);\ \tau_{xz} = \tau_{yz} = 0$$

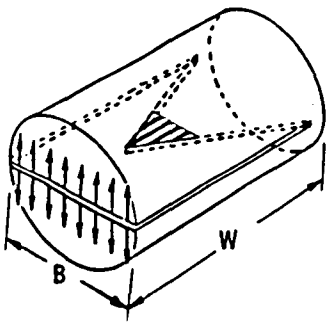
K_I IS THE "STRESS INTENSITY FACTOR"

K_{Ic} IS THE "FRACTURE TOUGHNESS"

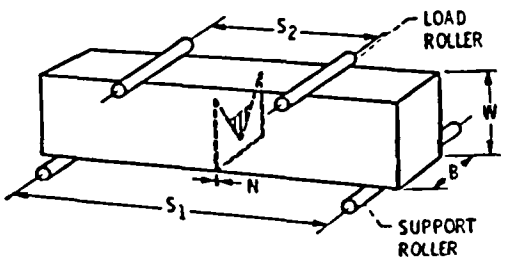
CHEVRON-NOTCH SPECIMENS



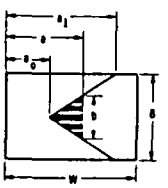
SHORT BAR



SHORT ROD



FOUR-POINT BEND

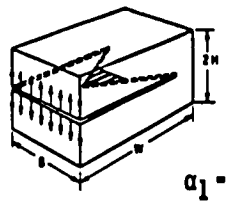


CRACK PLANE SECTION

THEORETICAL BASIS FOR CHEVRON-NOTCH SPECIMEN K_{IC} MEASUREMENT

AVAILABLE ENERGY FOR EXTENSION OF CRACK BY Δa:

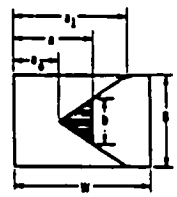
$$\Delta U = \frac{P^2}{2W} \cdot \frac{dC_{tr}}{d\alpha} \cdot \Delta a$$



NECESSARY ENERGY FOR EXTENSION OF CRACK BY Δa:

$$\Delta \overline{W} = G_{Ic} \cdot b \cdot \Delta a = \frac{K_{Ic}^2}{E} \cdot b \cdot \Delta a$$

$\alpha_1 = a_1/W$
$\alpha = a/W$
$\alpha_0 = a_0/W$

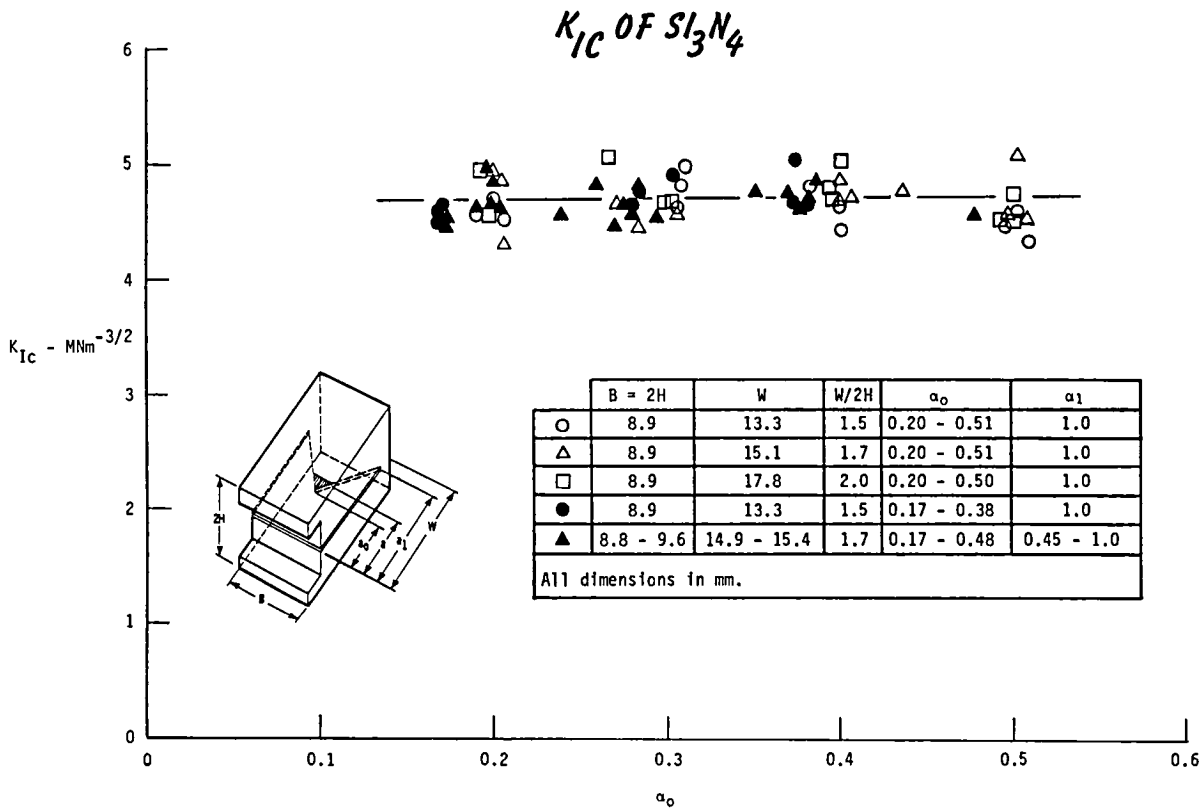


DURING CRACK EXTENSION $\Delta U = \Delta \overline{W}$, AND:

$$K_{Ic} = P\left[\frac{E}{2bW}\frac{dC_{tr}}{d\alpha}\right]^{1/2}$$

AND SINCE $b = B\left[\frac{a - a_0}{a_1 - a_0}\right] = B\left[\frac{\alpha - \alpha_0}{\alpha_1 - \alpha_0}\right]$

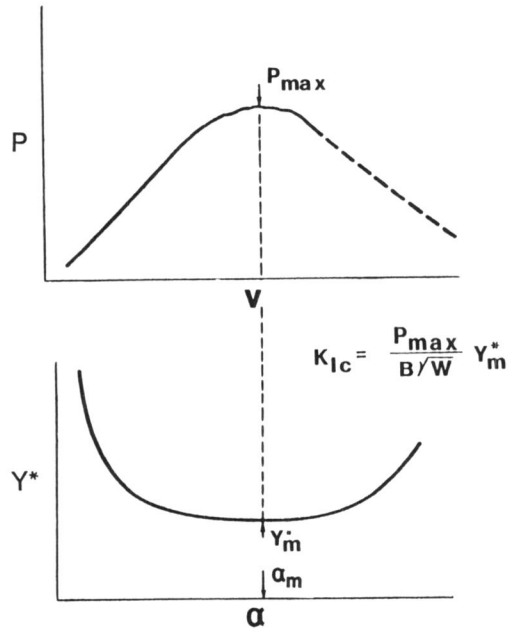
$$K_{Ic} = P\left[\frac{E}{2WB\left(\frac{\alpha - \alpha_0}{\alpha_1 - \alpha_0}\right)}\frac{dC_{tr}}{d\alpha}\right]^{1/2} = \frac{P}{B\sqrt{W}}\left[\frac{EB}{2}\frac{dC_{tr}}{d\alpha}\left(\frac{\alpha_1 - \alpha_0}{\alpha - \alpha_0}\right)\right]^{1/2} = \frac{P}{B\sqrt{W}}Y^*$$



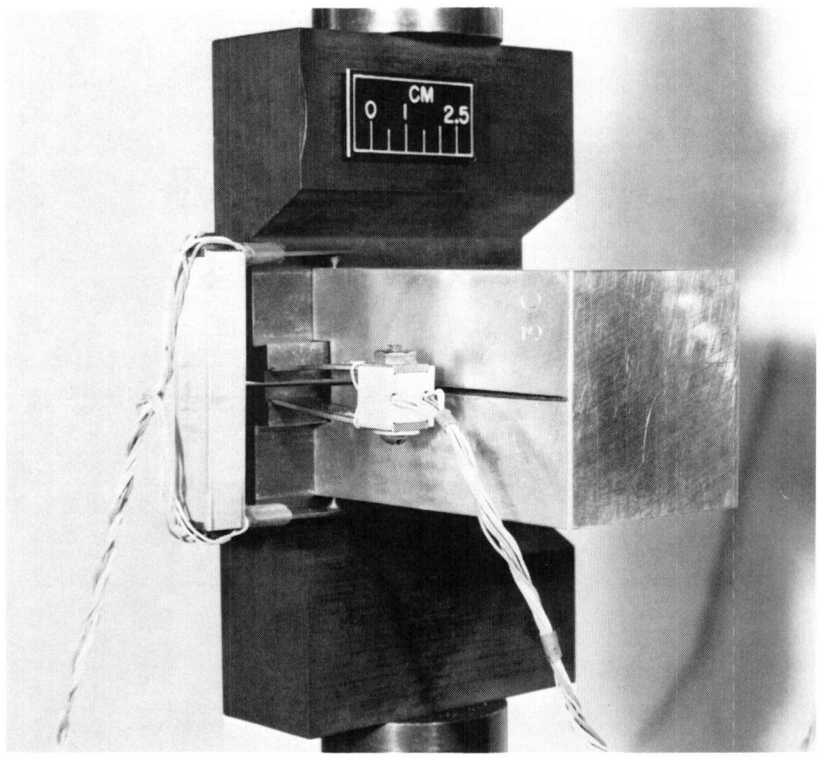
	B = 2H	W	W/2H	α_o	α_1
○	8.9	13.3	1.5	0.20 - 0.51	1.0
△	8.9	15.1	1.7	0.20 - 0.51	1.0
□	8.9	17.8	2.0	0.20 - 0.50	1.0
●	8.9	13.3	1.5	0.17 - 0.38	1.0
▲	8.8 - 9.6	14.9 - 15.4	1.7	0.17 - 0.48	0.45 - 1.0

All dimensions in mm.

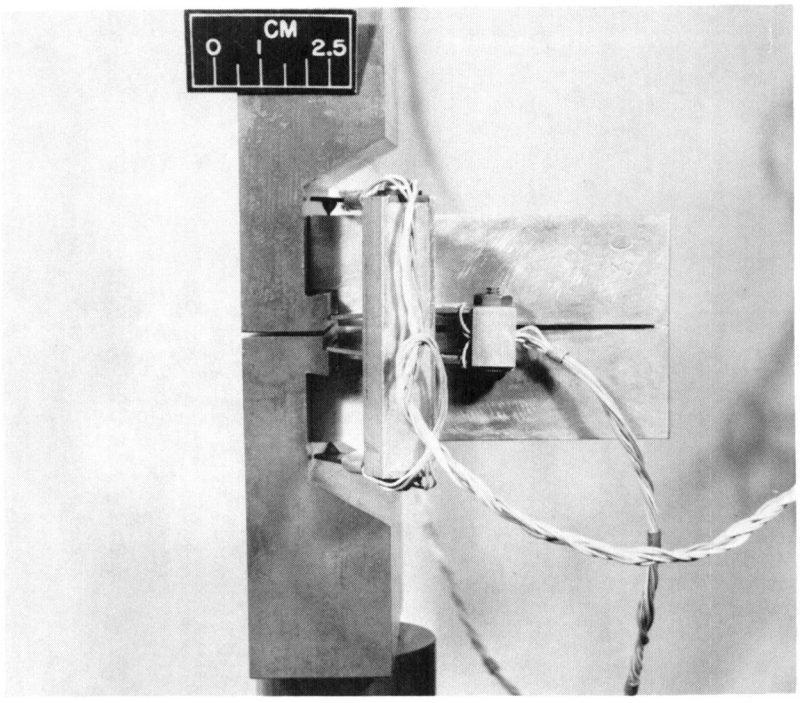
CHEVRON-NOTCH SPECIMEN K_{Ic} FROM P_{max} AND Y^*_m



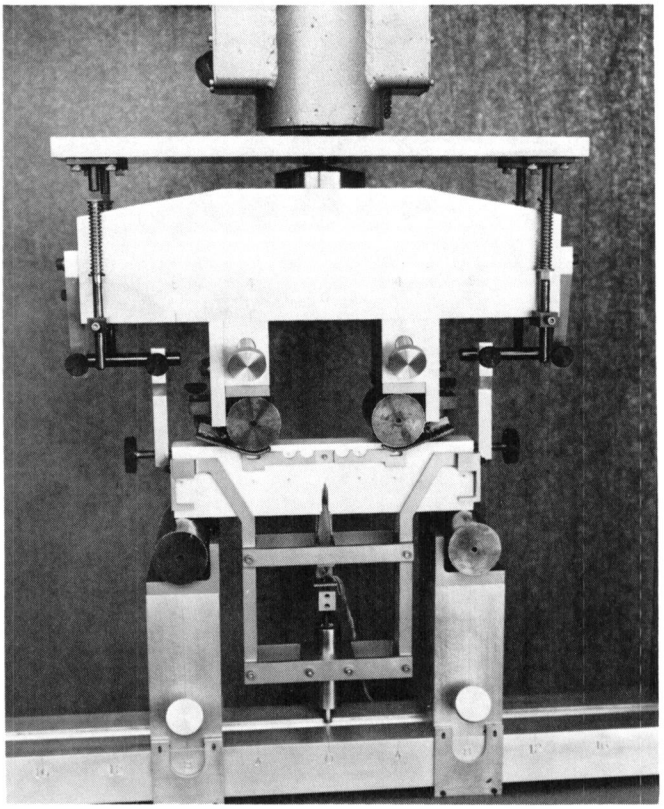
CHEVRON-NOTCH SPECIMEN K CALIBRATION SETUP



CHEVRON-NOTCH SPECIMEN K CALIBRATION SETUP

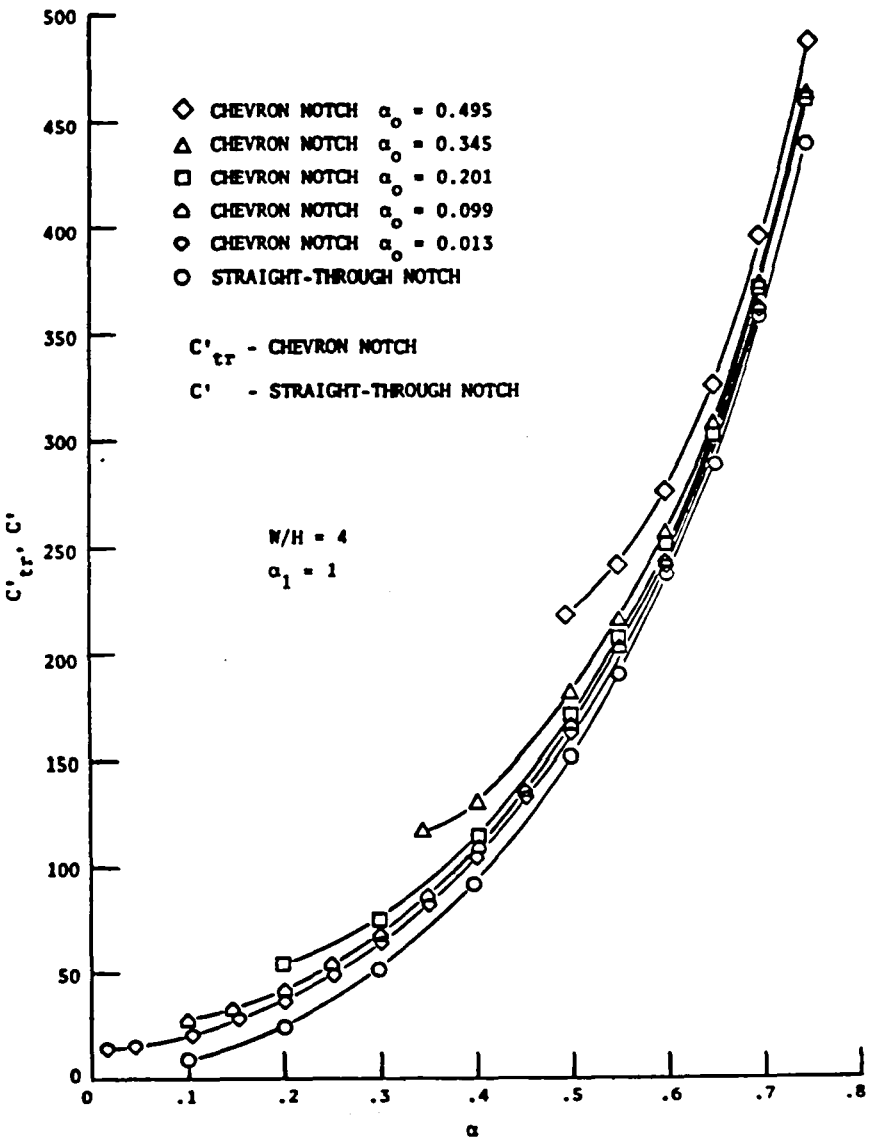


CHEVRON-NOTCH SPECIMEN K CALIBRATION SETUP

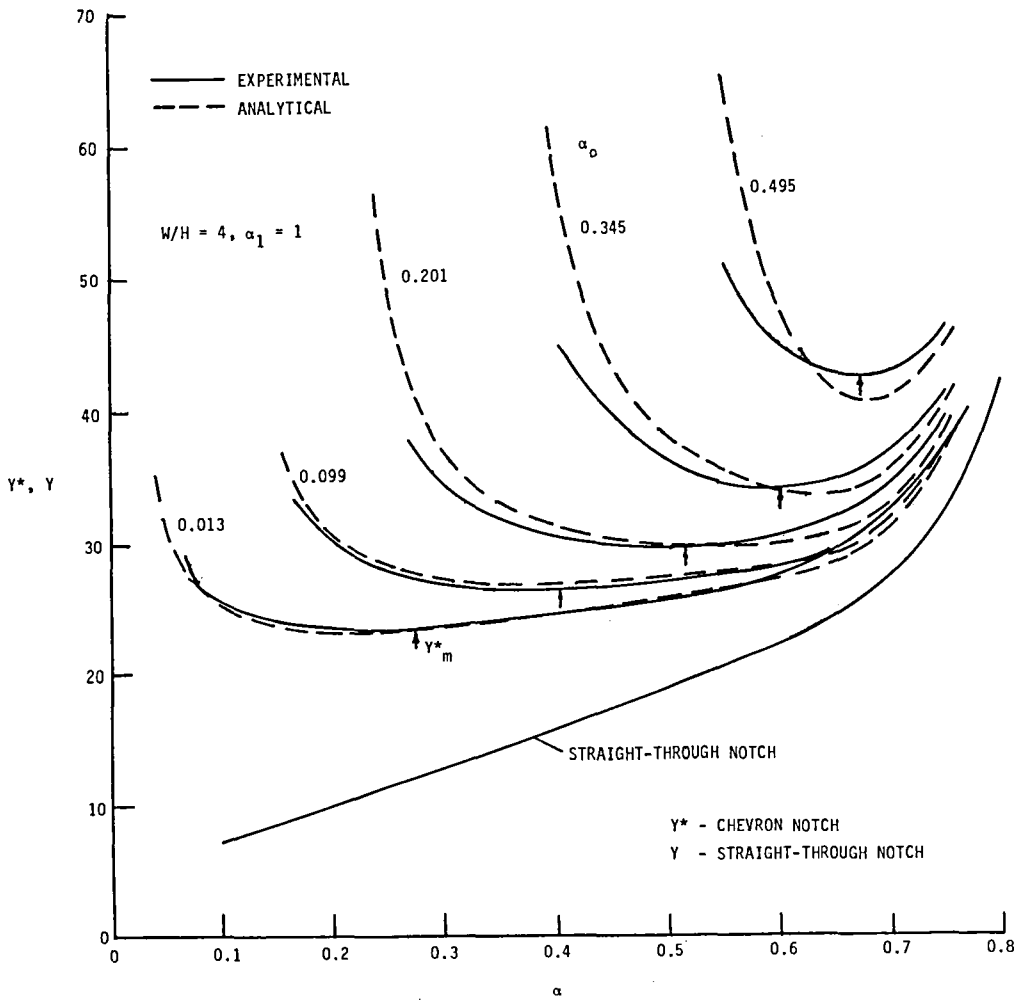


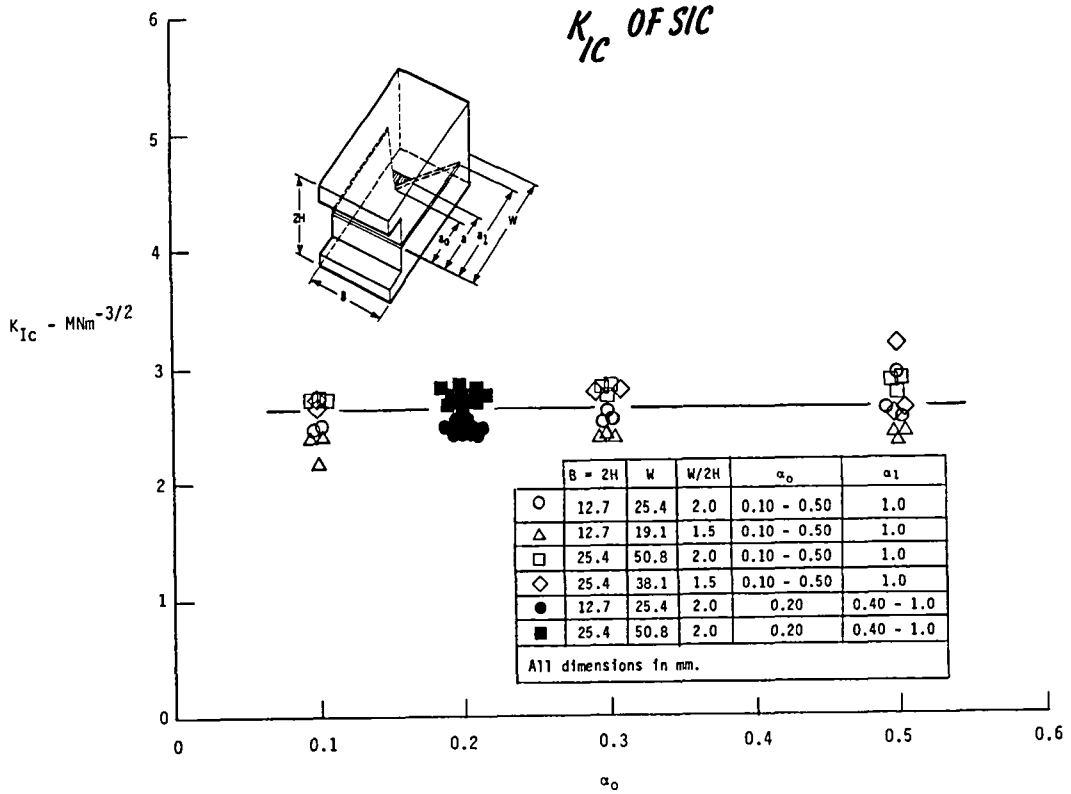
CHEVRON-NOTCH SPECIMEN K CALIBRATION SETUP

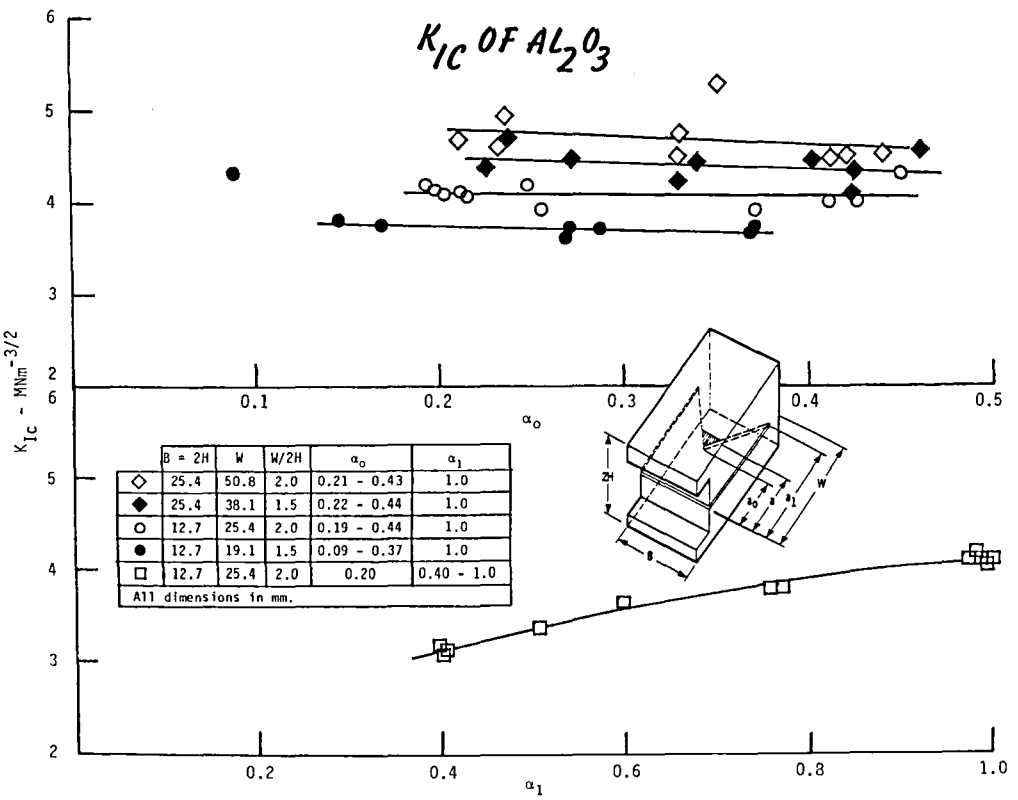
CHEVRON-NOTCH SHORT BAR SPECIMEN DIMENSIONLESS COMPLIANCE



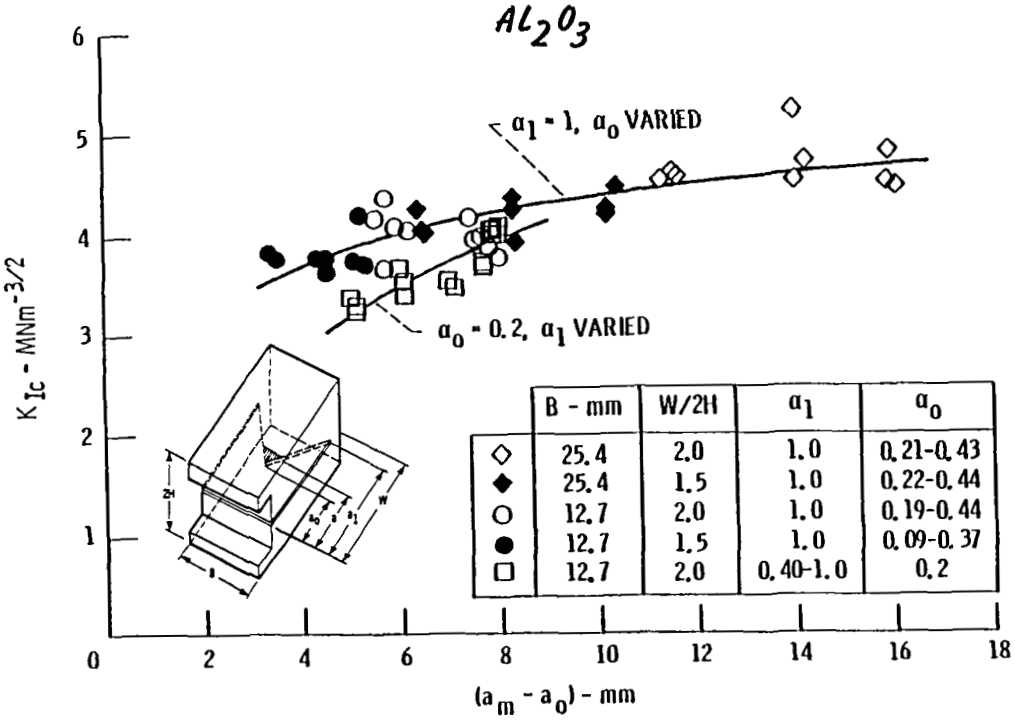
CHEVRON-NOTCH SHORT BAR SPECIMEN STRESS INTENSITY FACTOR COEFFICIENTS




K_{IC} OF SIC
K_{Ic} - MNm$^{-3/2}$
α_o
B = 2H | W | W/2H | α_o | α_1
12.7 | 25.4 | 2.0 | 0.10 - 0.50 | 1.0
12.7 | 19.1 | 1.5 | 0.10 - 0.50 | 1.0
25.4 | 50.8 | 2.0 | 0.10 - 0.50 | 1.0
25.4 | 38.1 | 1.5 | 0.10 - 0.50 | 1.0
12.7 | 25.4 | 2.0 | 0.20 | 0.40 - 1.0
25.4 | 50.8 | 2.0 | 0.20 | 0.40 - 1.0
All dimensions in mm.

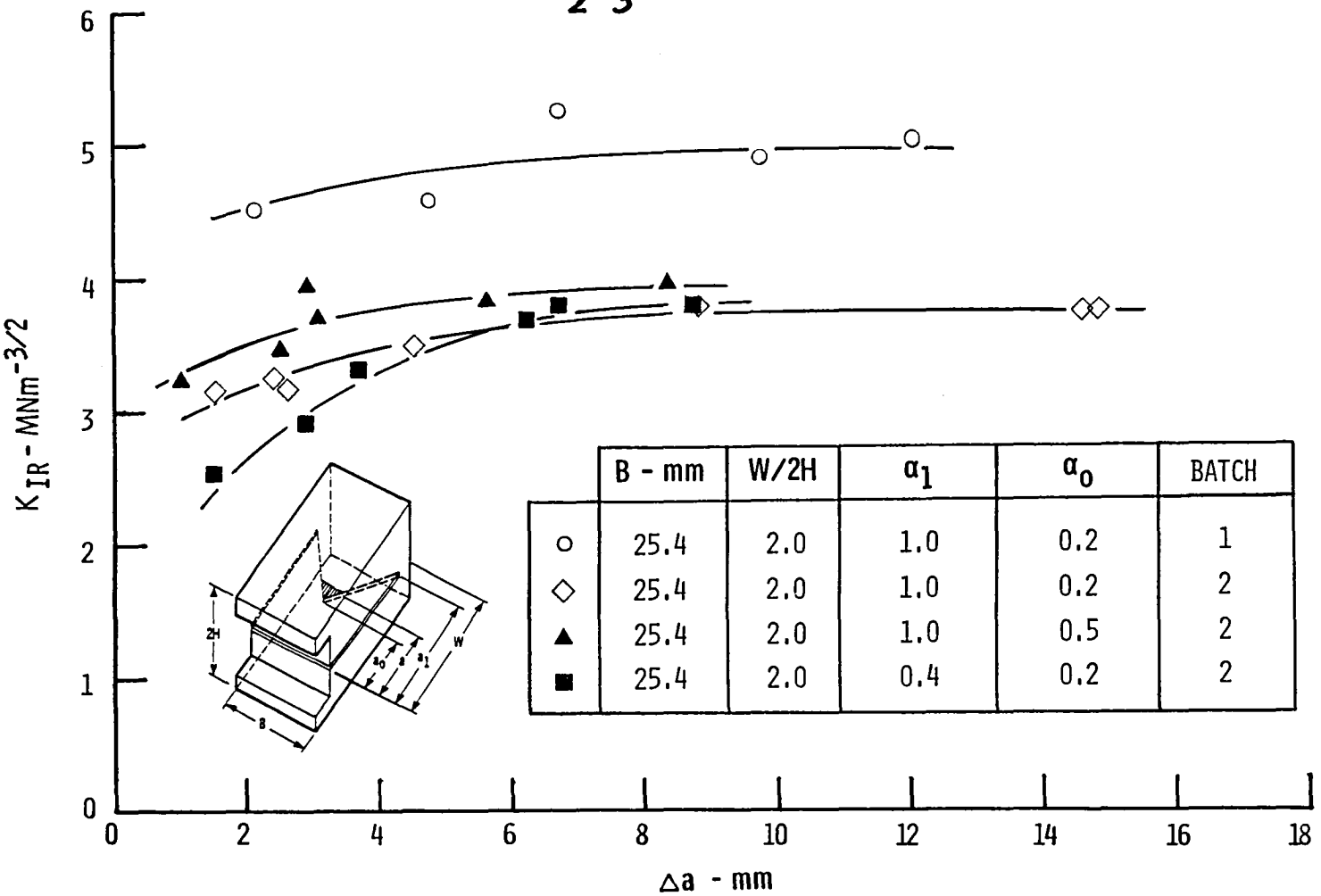

K_{IC} OF AL_2O_3
K_{Ic} - MNm$^{-3/2}$
α_o
α_1
B = 2H | W | W/2H | α_o | α_1
25.4 | 50.8 | 2.0 | 0.21 - 0.43 | 1.0
25.4 | 38.1 | 1.5 | 0.22 - 0.44 | 1.0
12.7 | 25.4 | 2.0 | 0.19 - 0.44 | 1.0
12.7 | 19.1 | 1.5 | 0.09 - 0.37 | 1.0
12.7 | 25.4 | 2.0 | 0.20 | 0.40 - 1.0
All dimensions in mm.

VARIATION IN K_{IC} WITH CRACK EXTENSION TO P_{MAX}



	B - mm	W/2H	a_1	a_0
◇	25.4	2.0	1.0	0.21-0.43
◆	25.4	1.5	1.0	0.22-0.44
○	12.7	2.0	1.0	0.19-0.44
●	12.7	1.5	1.0	0.09-0.37
□	12.7	2.0	0.40-1.0	0.2

Al_2O_3 R-CURVES



	B - mm	W/2H	α_1	α_0	BATCH
○	25.4	2.0	1.0	0.2	1
◇	25.4	2.0	1.0	0.2	2
▲	25.4	2.0	1.0	0.5	2
■	25.4	2.0	0.4	0.2	2

STRUCTURAL CERAMICS RESEARCH

J.I. Mueller, R.J.H. Bollard, and R.C. Bradt
University of Washington
Seattle, Washington

OUTLINE

CERAMIC RESEARCH AT U. OF W.

BRITTLE MATERIALS DESIGN PROGRAM

NASA PROGRAM RESEARCH AT U. OF W.

STRUCTURAL CERAMIC RESEARCH at U. of W.

AKSAY, I.	MSE	powder processing, sintering
BERG, J.	ChE	colloidal studies
BJORKSTAM, J.	EE	NDE/NDT
BOLLARD, R.J.H.	AA	evaluation, design
BRADT, R.	MSE	mechanical properties
DASH, G.	PHY	thermal conditions
EMERY, A.	ME	thermal stresses
FISCHBACH, D.	MSE	fiber composite, carbon
HARTZ, B.	CE	design
KIKUCHI, R.	MSE	theoretical modeling
KOBAYASHI, A.	ME	mechanical prop., dynamic fracture
LIN, K.	AA	elast. mechanical comp.
MILLER, A.	MSE	processing, environ. effects
RAMULU, M.	ME	dynamic fracture, machining
RAO, Y.	MSE	nitridation Si
REED, D.	CE	design
SARIKAYA, M.	MSE	characterization
SCOTT, W.	MSE	oxidation
STOEBE, T.	MSE	nitridation, defects
TAGGART, R.	ME	design
TAYA, M.	ME	comp. mechanics
WHITTEMORE, O	MSE	processing

BRITTLE MATERIALS DESIGN PROGRAM (COURSE)

BRITTLE MATERIALS

PROCESSING of CERAMICS

ELASTICITY

MECHANICAL CHARACTERIZATION

MICROSTRUCTURE/MECHANICAL PROPERTIES

ENGINEERING PROPERTIES of CERAMICS

STRENGTH and FAILURE THEORIES

NDE/NDT

DESIGN of COMPONENTS

LABORATORY (PP) COMPONENT MANUFACTURE

CURRENT NASA RESEARCH PROGRAM AT UW

I. PROCESSING AND CHARACTERIZATION

STOEBE - Lattice Defects in Si_3N_4

RAO - Nitridation of Si

AKSAY - Powder Consolidation by Injection Molding

SCOTT - Oxidation Resistance of Si_3N_4

II. MECHANICAL PROPERTIES

MILLER - Environmental Effects on Si_3N_4, SiC

EMERY - Thermal Fracture

KOBAYASHI - Impact, Erosion, Dynamic Fracture

BOLLARD - Evaluation of Mechanical Tests

BRADT/REED - Micromechanical Stresses

PROPOSED 86/87 CERAMIC/COMPOSITES RESEARCH TOPICS

AKSAY - POWDER PROCESSING

RAO - NITRIDATION

MILLER -COMPOSITE NITRIDATION

BERG - COLLOIDAL PROCESSING OF COMPOSITES

EMERY - THERMAL PROPERTIES

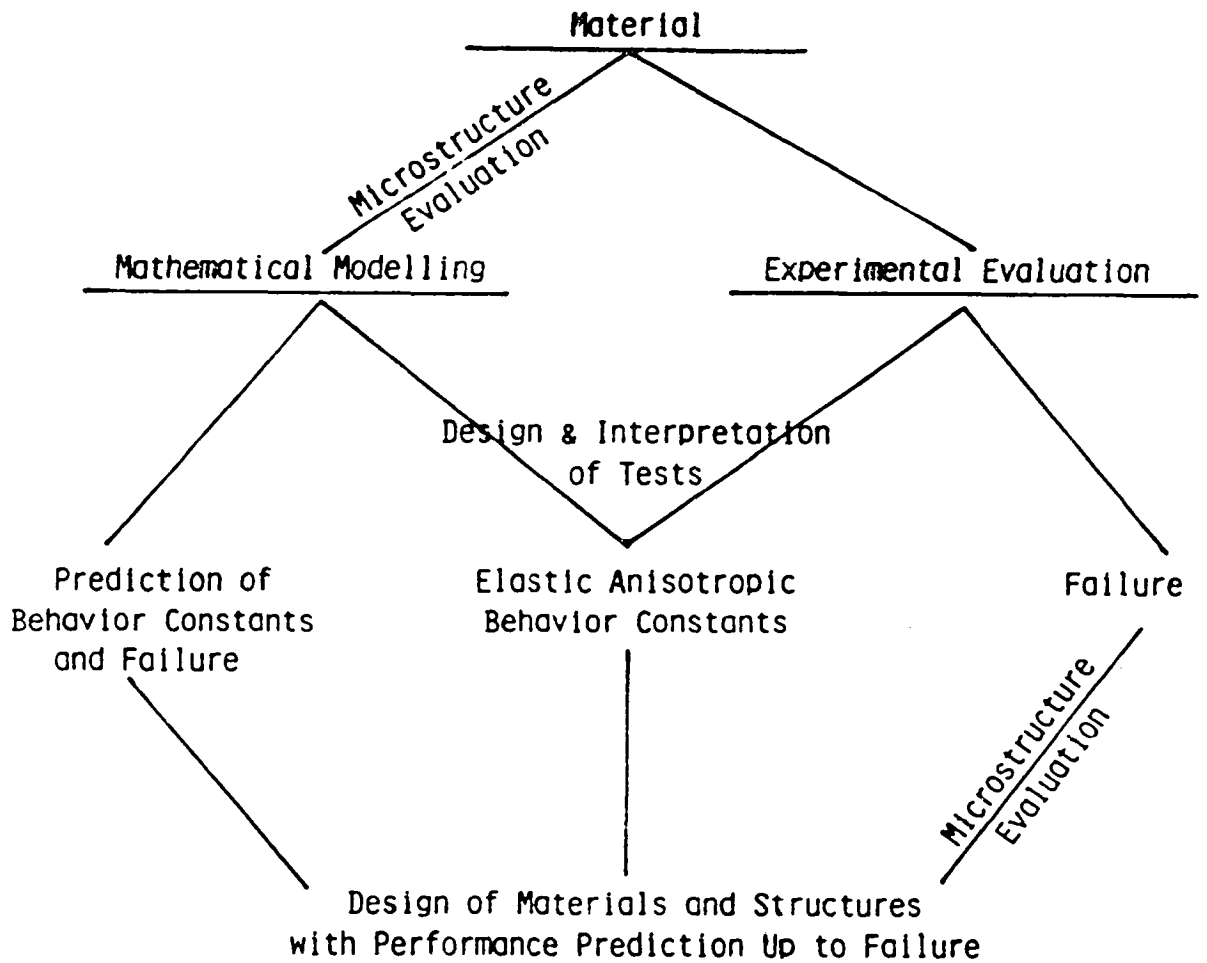
KOBAYASHI - DYNAMIC MECHANICAL PROPERTIES

TAYA - THERMAL CYCLING FATIGUE

BRADT/REED - ANISOTROPIC RESIDUAL STRESSES

BOLLARD - MECHANICAL CHARACTERIZATION

COMPOSITE CHARACTERIZATION



IMPROVED SILICON CARBIDE FOR ADVANCED HEAT ENGINES*

Thomas J. Whalen and J.A. Mangels
Ford Motor Company

This report describes work performed in the first year of the program conducted for NASA to develop silicon carbide materials of high strength and to form components of complex shape and high reliability. The approach has been to adapt a beta-SiC powder and binder system to the injection molding process and to develop procedures and process parameters capable of providing a sintered silicon carbide material with improved properties.

The initial effort has been to characterize the baseline precursor materials (beta silicon carbide powder and boron and carbon sintering aids), develop mixing and injection molding procedures for fabricating test bars, and characterize the properties of the sintered materials. Parallel studies of various mixing, dewaxing, and sintering procedures have been performed in order to distinguish process routes for improving material properties.

A total of 276 MOR bars of the baseline material have been molded, and 122 bars have been fully processed to a sinter density of approximately 95 percent. The material has a mean MOR room temperature strength of 43.3 ksi (299 mPa), a Weibull characteristic strength of 45.8 ksi (315 mPa) and a Weibull modulus of 8.0. Mean values of the MOR strengths at 1000 °C, 1200 °C and 1400 °C are 41.4 ksi, 43.2 ksi and 47.2 ksi, respectively. Strength controlling flaws in this material were found to consist of regions of high porosity and were attributed to agglomerates originating in the initial mixing procedures.

New fluid mixing techniques have been developed which significantly reduce flaw size and improve the strength of the material. Initial MOR tests indicate the strength of the fluid-mixed material exceeds the baseline property by more than 33 percent.

Plans for the development of the fluid-mixing process to reduce flaw size and increase density and the optimization of sinter-body microstructure to increase toughness of the silicon carbide materials will be reviewed.

Contributions to this program were made by the following.

Ford Motor Company: R. Govila, B.N. Juterbock, J.A. Mangels, V. Mindroiu, L.R. Reatherford, S.S. Shinozaki, W. Trela, T.J. Whalen, R.M. Williams, and W.L. Winterbottom

NASA: S. Levine and N. Shaw

---

*Work performed under NASA Contract No. NAS3-24384

FIRST YEAR REVIEW

T. J. Whalen

J. A. Mangels

May 21, 1986

OBJECTIVE :

Develop High Strength, High Reliability Silicon Carbide Parts Having Complex Shapes by a Method Adaptable to Mass Production on an Economically Sound Basis.

APPROACH :

Adapt Powder and Binder System to Injection Molding Process and Develop Procedures and Optimize Process Parameters Leading to a Sintered Silicon Carbide Material with Improved Properties.

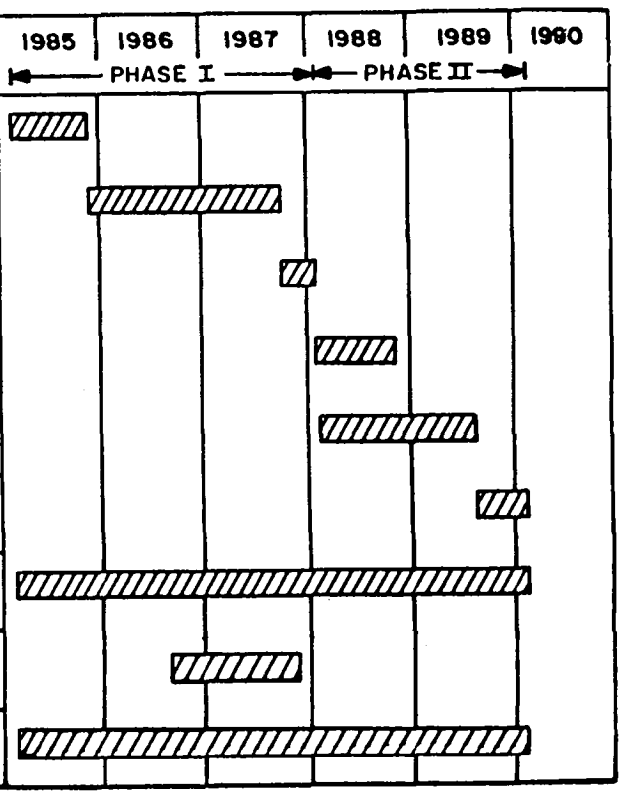
BENEFITS :

Silicon Carbide Parts for Advanced Gas Turbines and Other Heat Engines Would Permit Higher Temperature Operation with Resulting Fuel Efficiencies.

START / FINISH :

February, 1985 to February, 1988

TASK NO.	DESCRIPTION	% EFFORT
I	BASELINE CHARAC.	5
II	MOR MATRIX	25
III	OPTIMIZED MOR	5
IV	BASELINE LRG. SHP.	5
V	LRG. SHP. MATRIX	25
VI	OPTIM. LRG. SHP.	10
VII	MAT'L./PROC. IMP.	15
VIII	T'CHARGE. FAB.	5
IX	RPTS./PROJ. MGMT.	5



Timing Chart

OUTLINE

TASK I — T. J. WHALEN

* BASELINE POWDERS CHARACTERIZATION
* BASELINE COMPOSITION SELECTION
* BASELINE RESULTS

TASK VII AND PLANS — J. A. MANGELS

* PROCESSING AND COMPOSITION IMPROVEMENTS
* PLANNING

TASK I

BASELINE CHARACTERIZATION

POWDERS

CHEMICAL ANALYSIS - BASELINE MATERIAL

ELEMENT	UF-SiC	BORON	CARBON
C	30.4[1]	0.36	98.6
O	0.85	1.71	1.12
Al	0.046	0.040	
Fe	0.043	0.17	<0.005
Ca	0.019	0.046	
Mg	0.015	0.55	
Ti	0.005	0.047	
Zr	0.005		
S			0.25

[1] Weight Percent

B.E.T. SURFACE AREA

As Received Powders for Baseline Bars

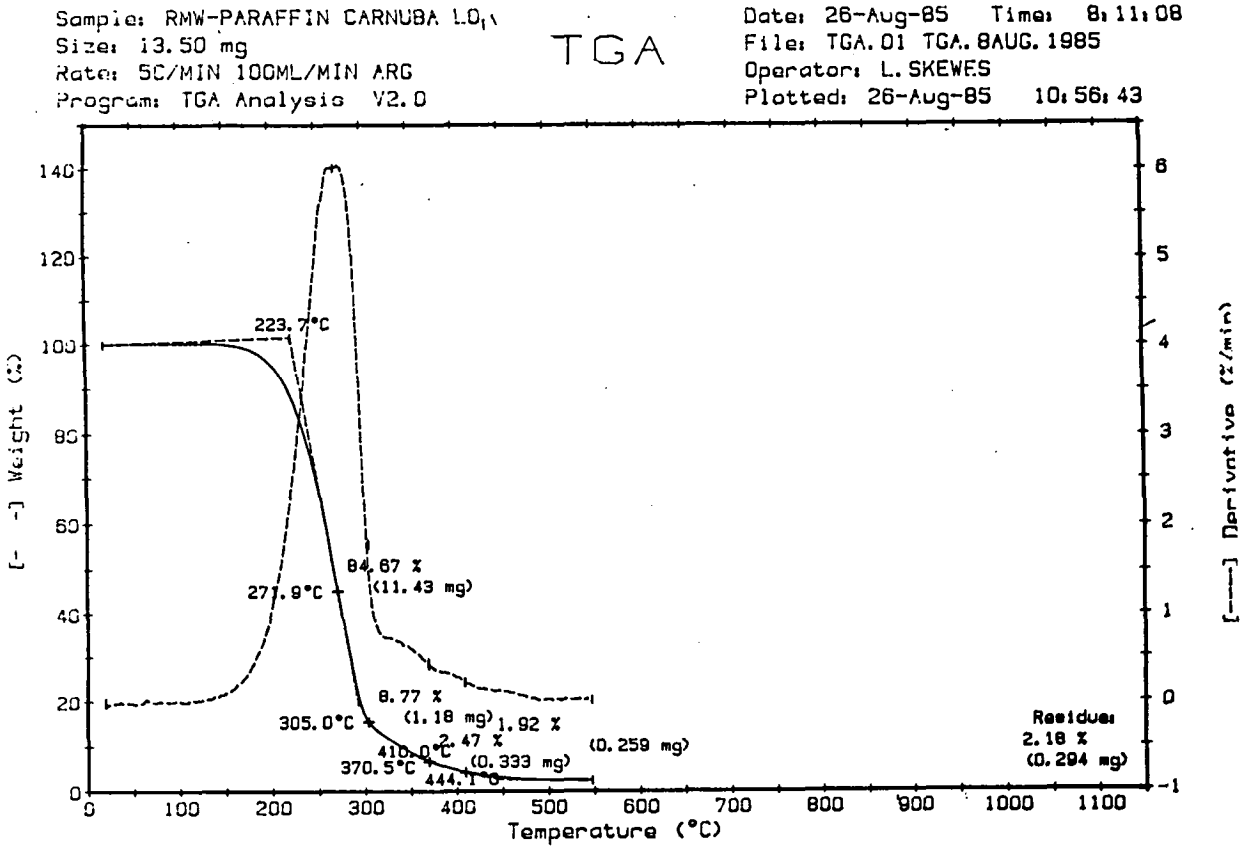
Ibiden UF	Lot 0166	SiC	21.5 M^2/g
Starck	Lot S-3506	B	12.1 M^2/g
Monsanto	Lot TL-246	C	53.1 M^2/g

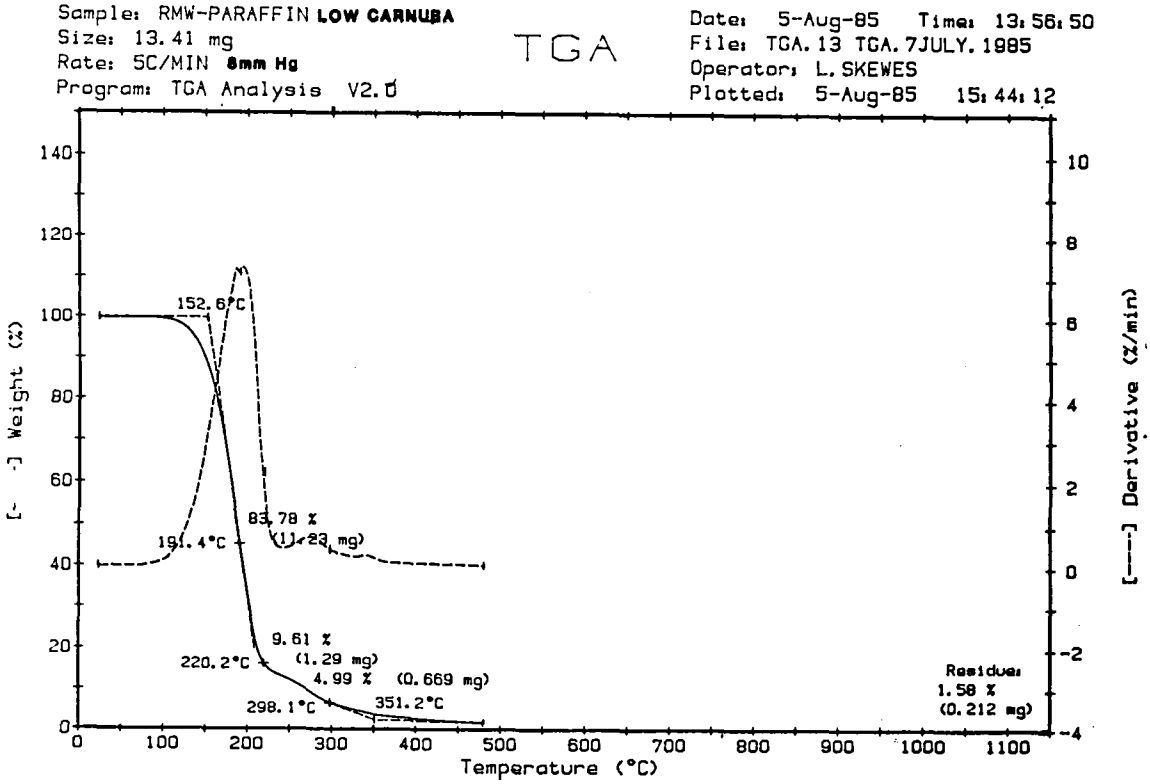
PARTICLE DIAMETER, SPECIFIC GRAVITY, PACK DENSITY,

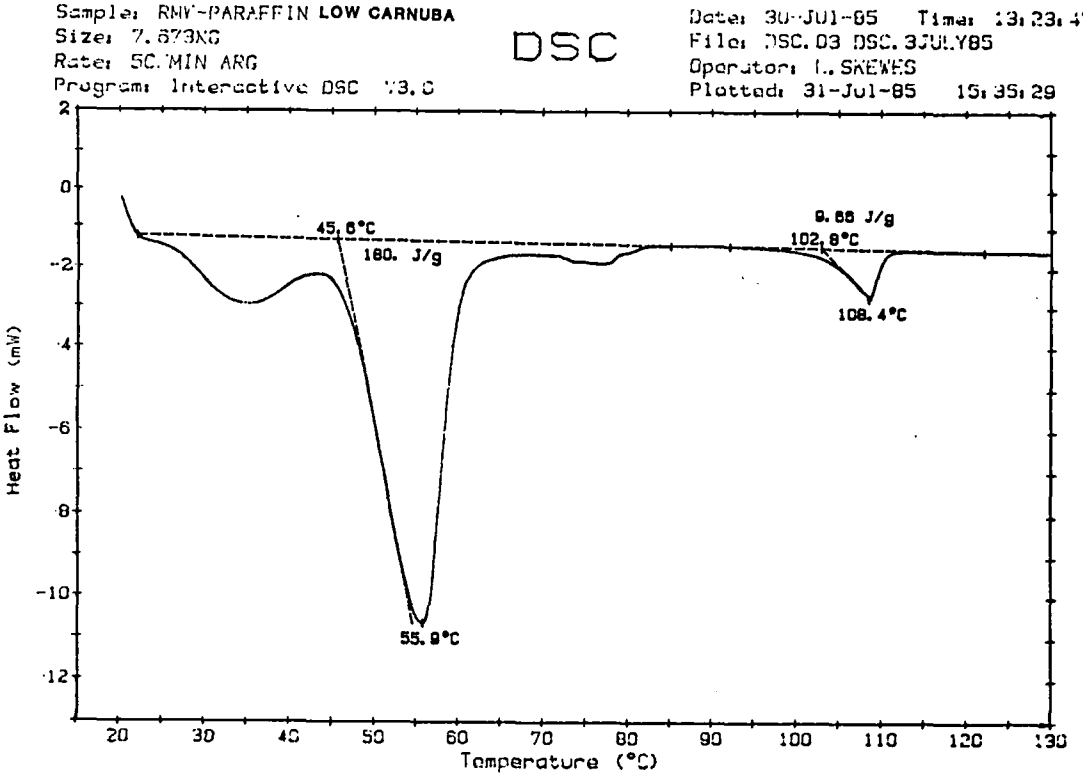
AND POLYPHASE ANALYSIS OF SiC POWDER FOR BASELINE BARS

Particle Diameter	Volume Dist.	Frequency Dist
UF Lot 0166		
Median	1.05	0.61
Mode	1.16	0.64
Geometric Mean	1.04	0.59
Arithmetic Mean	1.18	0.65

Specific Gravity	3.161 gm/cm³
Pack Density	0.787 gm/cm³
X-ray Polyphase Analysis	
3C Phase	84.0 %
Disordered Phase	16.0 %

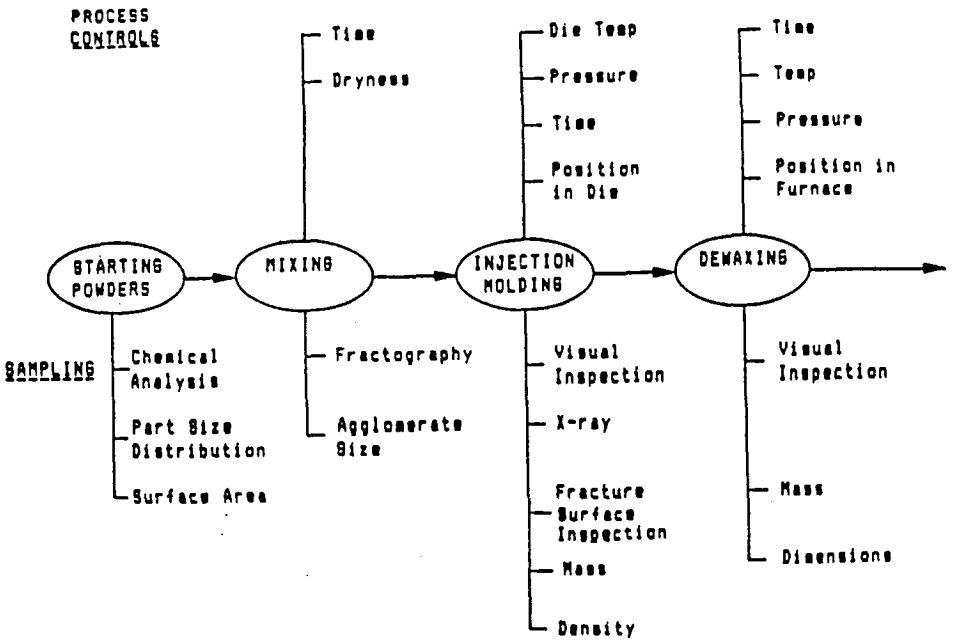


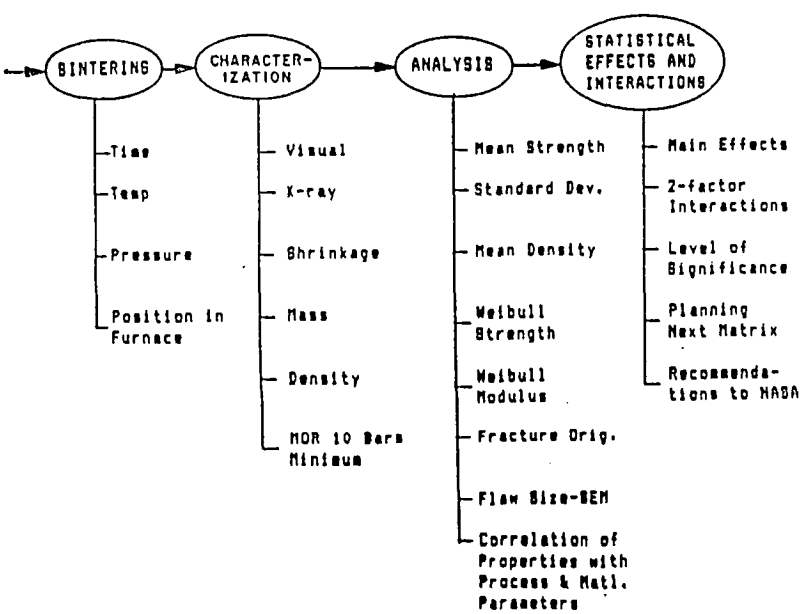

Sample: RMW-PARAFFIN LOW CARNUBA
Size: 13.41 mg
Rate: 5C/MIN 8mm Hg
Program: TGA Analysis V2.0
TGA
Date: 5-Aug-85 Time: 13:56:50
File: TGA.13 TGA.7JULY.1985
Operator: L. SKEWES
Plotted: 5-Aug-85 15:44:12
152.6°C
191.4°C
83.78 %
(11.23 mg)
9.61 %
220.2°C
(1.29 mg)
4.99 %
(0.669 mg)
298.1°C
351.2°C
Residue:
1.58 %
(0.212 mg)
[- -] Weight (%)
[——] Derivative (%/min)
Temperature (°C)


Sample: RMW-PARAFFIN LOW CARNUBA
Size: 7.673MG
Rate: 5C/MIN ARC
Program: Interactive DSC V3.0
DSC
Date: 30-Jul-85 Time: 13:23:47
File: DSC.03 DSC.30JULY85
Operator: L. SKEWES
Plotted: 31-Jul-85 15:35:29
45.6°C
180. J/g
9.88 J/g
102.8°C
108.4°C
55.9°C
Heat Flow (mW)
Temperature (°C)

TASK I

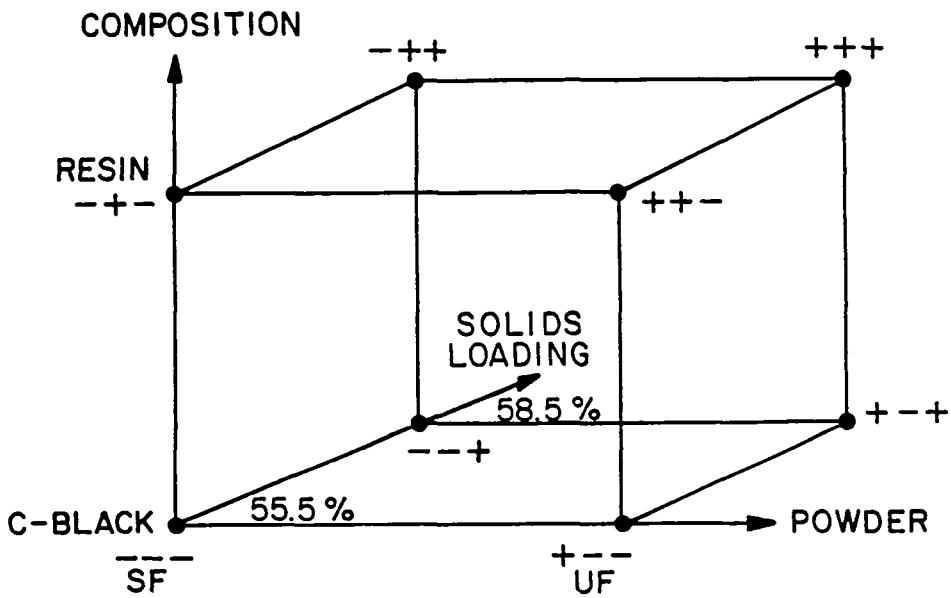
BASELINE CHARACTERIZATION PROCESS





2^3 EXPERIMENT TO

DETERMINE BASELINE COMPOSITION



2^3 BASELINE EXPERIMENT

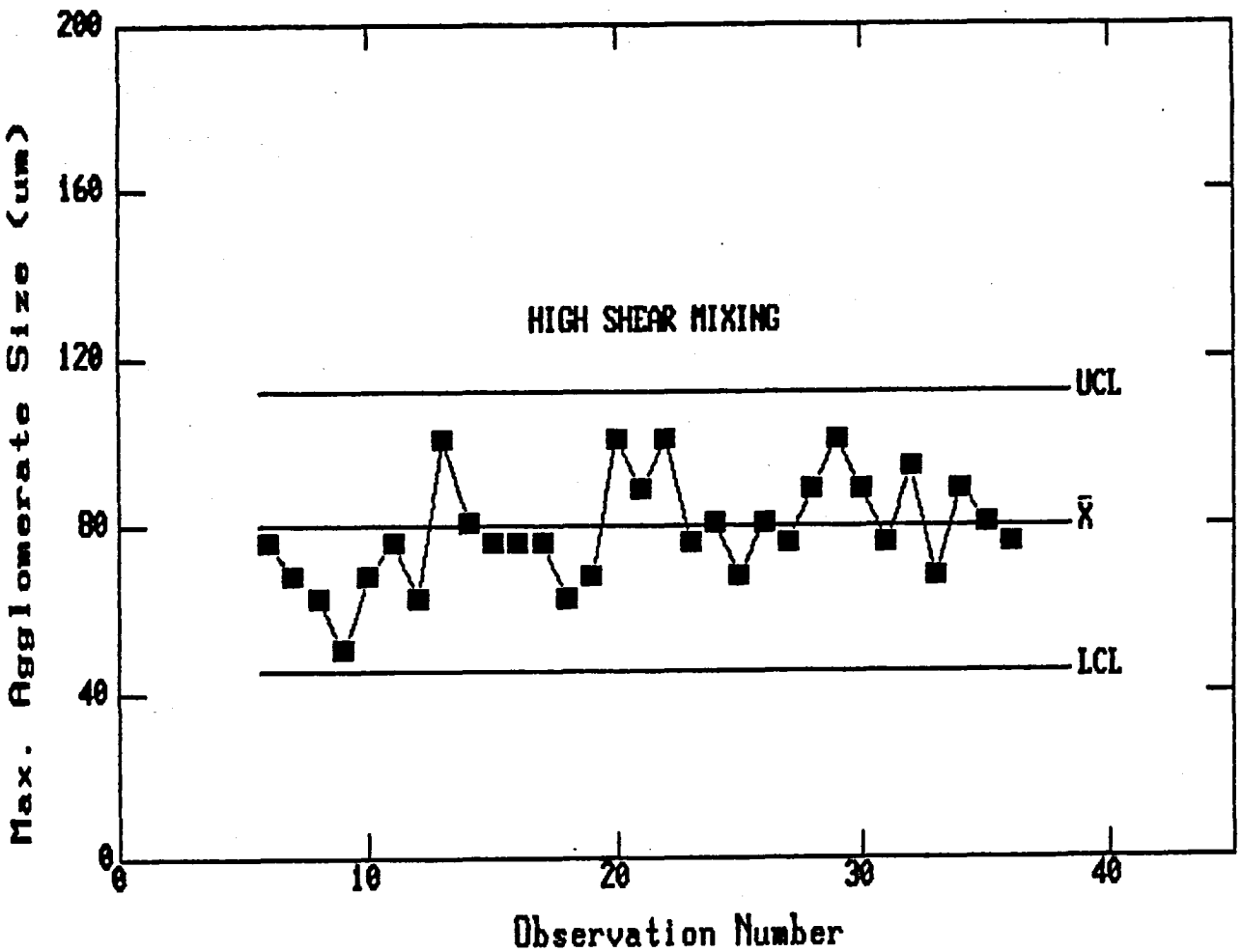
NASA #	SOLIDS LOADING LEVEL	CARBON SOURCE	SiC SOURCE	%T.D.
4	55.5	C-BLACK	UF	93
	58.5			94
5	55.5	C-BLACK	SF	91
	58.5			90
7	55.5	RESIN	UF	88
	58.5			--
8	55.5	RESIN	SF	88
	58.5			88

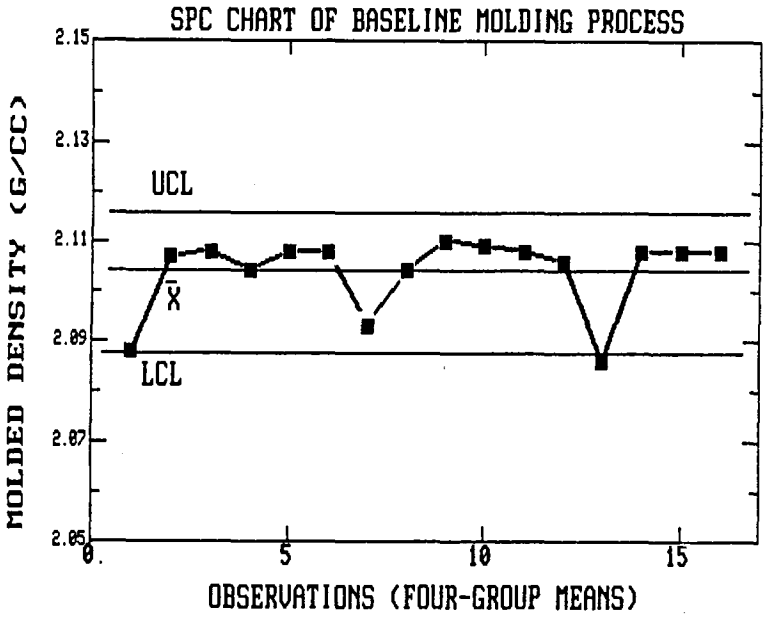
BASELINE COMPOSITION

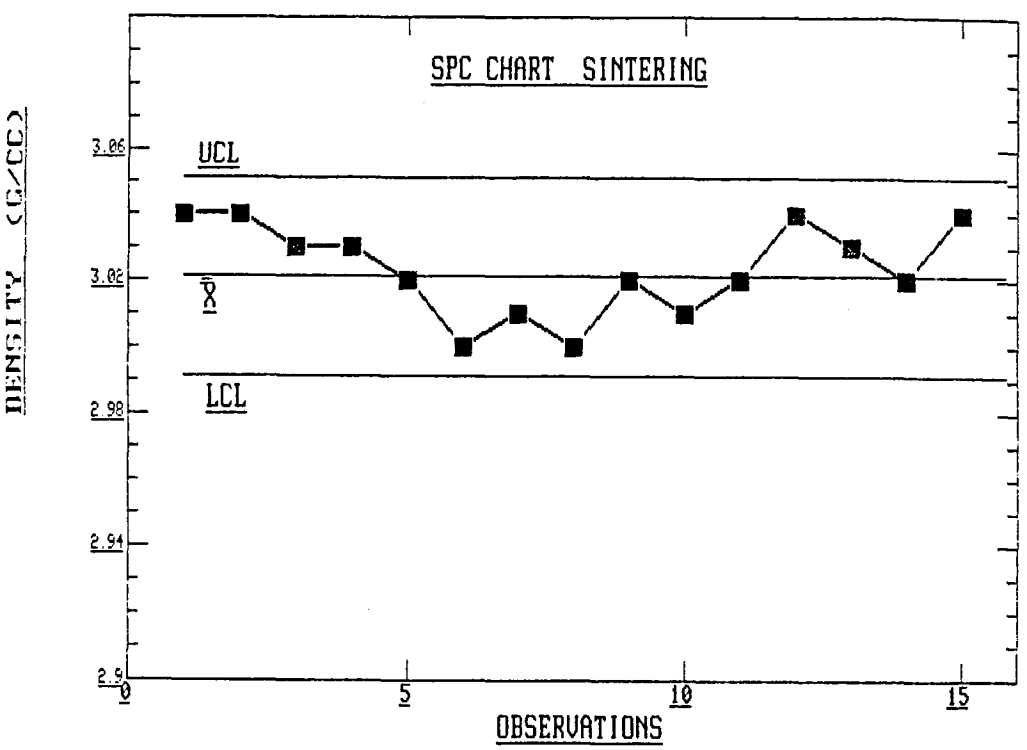
(From 2^3 Experiment)

2% C – 1%B – 97% SiC

55.5% Solids Loading




SPC CHART OF BASELINE MOLDING PROCESS
MOLDED DENSITY (G/CC)
2.15
2.13
2.11
2.09
2.07
2.05
UCL
LCL
0
5
10
15
OBSERVATIONS (FOUR-GROUP MEANS)


SPC CHART SINTERING
DENSITY (G/CC)
3.06
3.02
2.98
2.94
2.9
UCL
LCL
0
5
10
15
OBSERVATIONS

NASA 4G BASELINE

FRACTOGRAPHY AND X-RAY

M.O.R. BARS			FRACTURE ORIGIN	X-RAY
n	Ksi	S.D.		
5	39.9	6.2	3 - Sub Surface Porosity 2 - Surface Porosity	Large inclusions, Comp. Surface
5	41.1	5.3	4 - Sub Surface Porosity 1 - Surface Porosity	Large inclusions, Center Line
5	37.3	6.7	3 - Sub Surface Porosity 2 - Surface Porosity	Clean
5	42.3	3.9	3 - Sub Surface Porosity 2 - Surface Porosity	Small inclusions

M.O.R. BASELINE SUMMARY

Molded		276*	
X-ray acceptable		210	
Dewaxed (1 run)		127	
Sintered (3 runs)		122	
Room Temp. M.O.R.		30	
1000°C	FF	6	
	SR	6	(est)
1200°C	FF	6	
	SR	6	(est)
1400°C	FF	6	
	SR	6	(est)

* Number of M.O.R. Bars
FF Fast Fracture Test
SR Stress Rupture Test

TASK I

BASELINE CHARACTERIZATION

M.O.R. Results

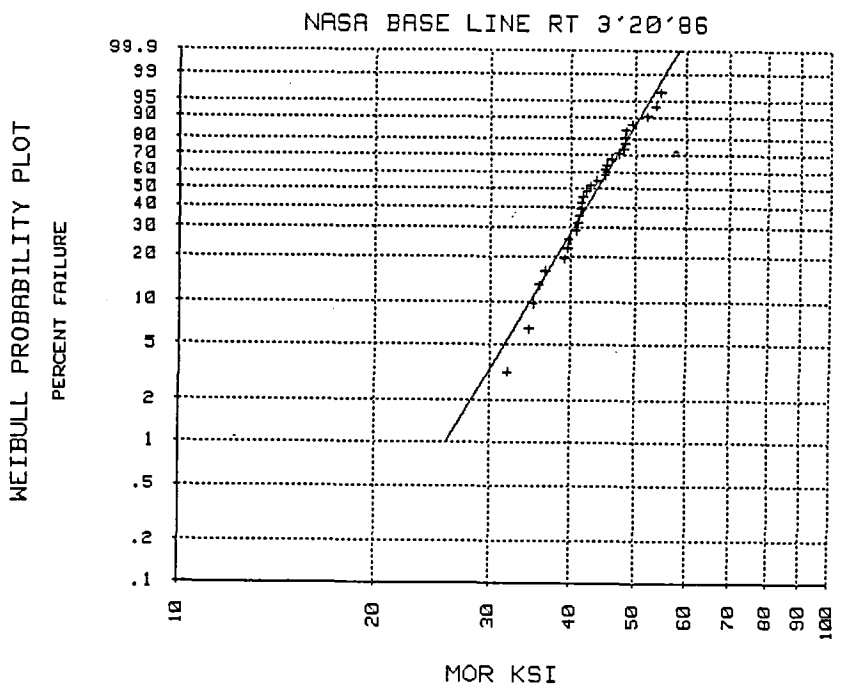
M.O.R. BASELINE RESULTS

		RT	1000°C	1200°C	1400°C
$\bar{x}$	Ksi	43.3	41.4	43.2	47.2
	mPa	(299)	(285)	(298)	(325)
n		30	6	6	6
θ	Ksi	45.8	WEIBULL SAMPLES TOO SMALL FOR ACCEPTABLE ACCURACY		
	mPa	(315)			
m		8			

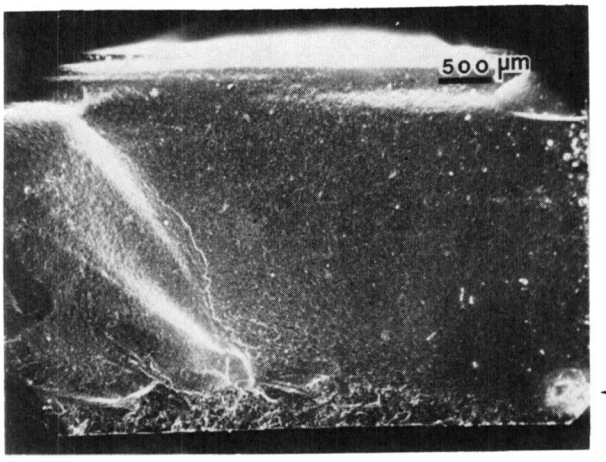
MOR KSI

NUMBER OF SAMPLES = 30.00
WEIBULL CHARACTERISTIC VALUE = 45.82
WEIBULL SLOPE = 7.97
DISTRIBUTION MEAN = 43.14
STANDARD DEVIATION = 6.43

PROB. OF FAILURE	EXPECTED VALUE
1.00	25.72
10.00	34.55
50.00	43.76
63.00	45.79
90.00	50.88
95.00	52.59
99.00	55.51
99.90	58.41

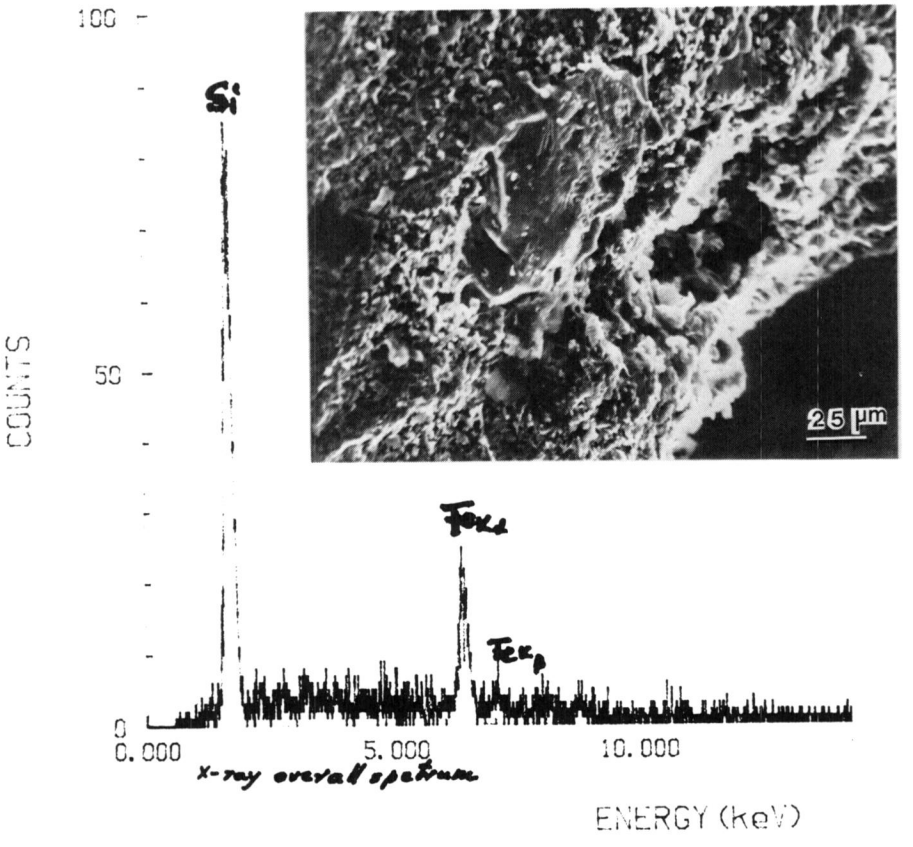


FRACTURE SURFACE
FLAW ORIGIN — IRON RICH



← FRACTURE ORIGIN

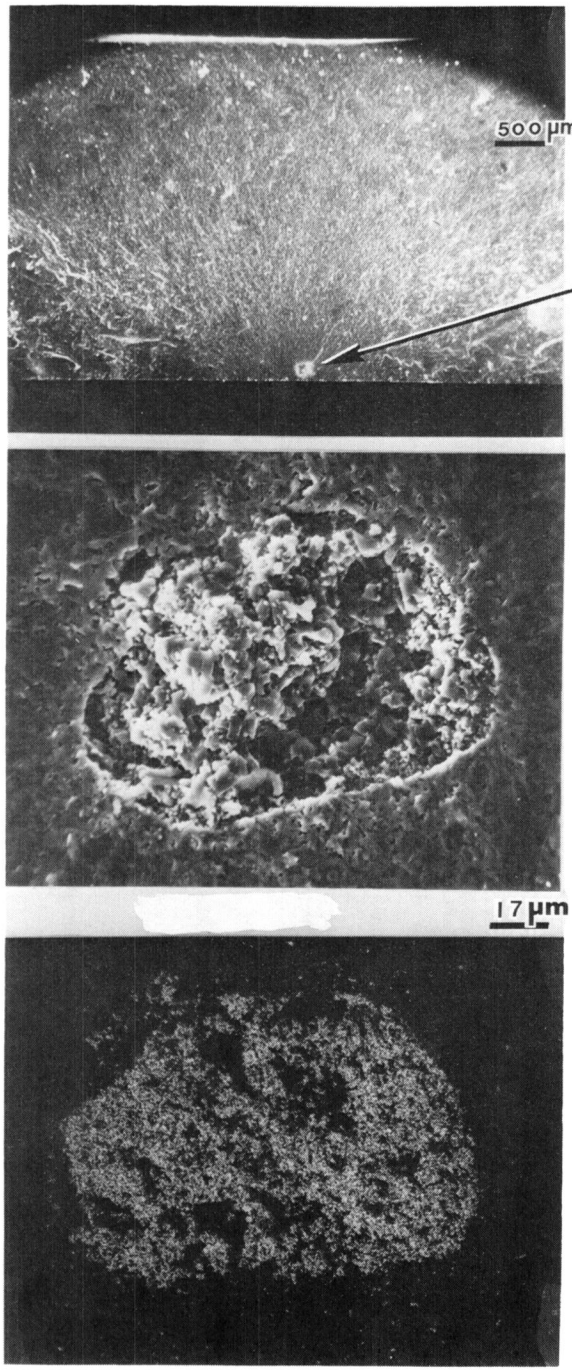
LT= 300 SECS



x-ray overall spectrum

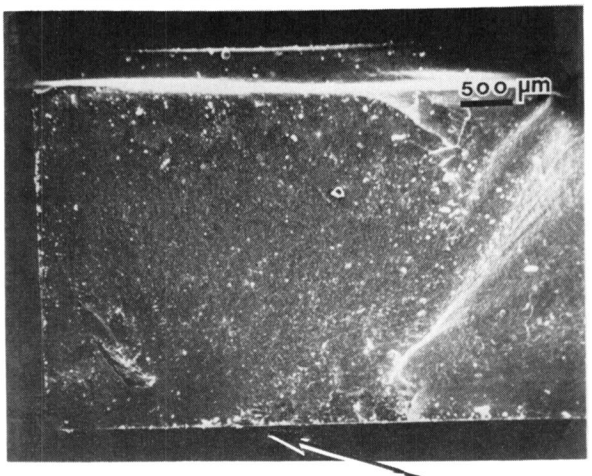
FRACTURE SURFACE

FLAW ORIGIN — BORON RICH



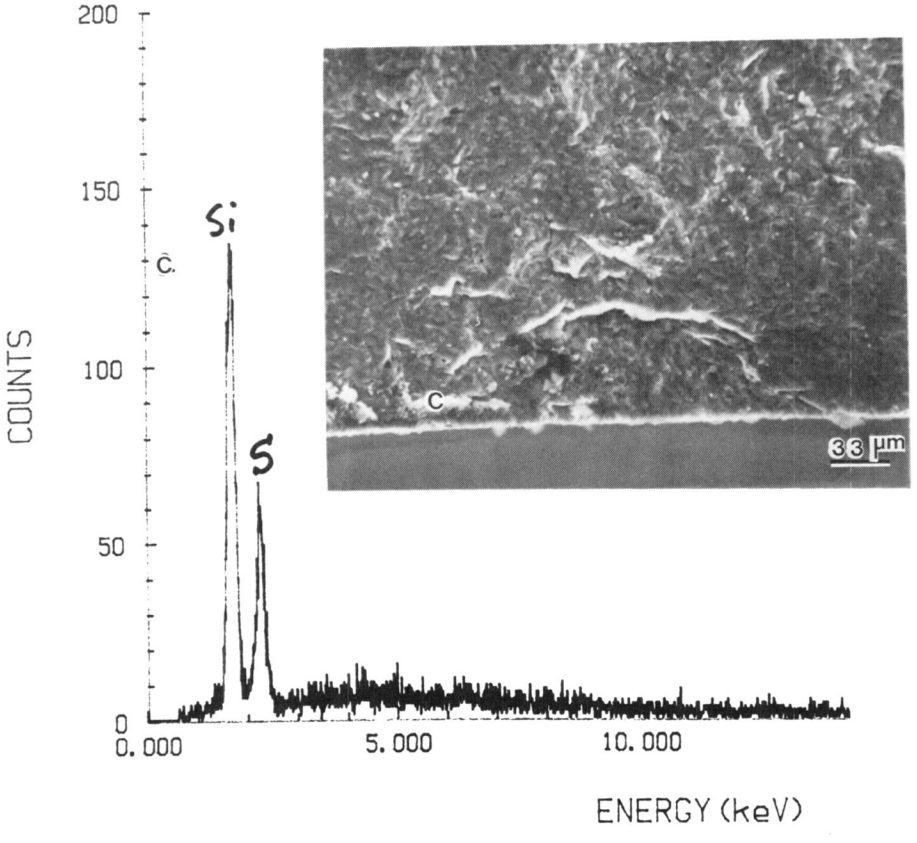
FRACTURE SURFACE

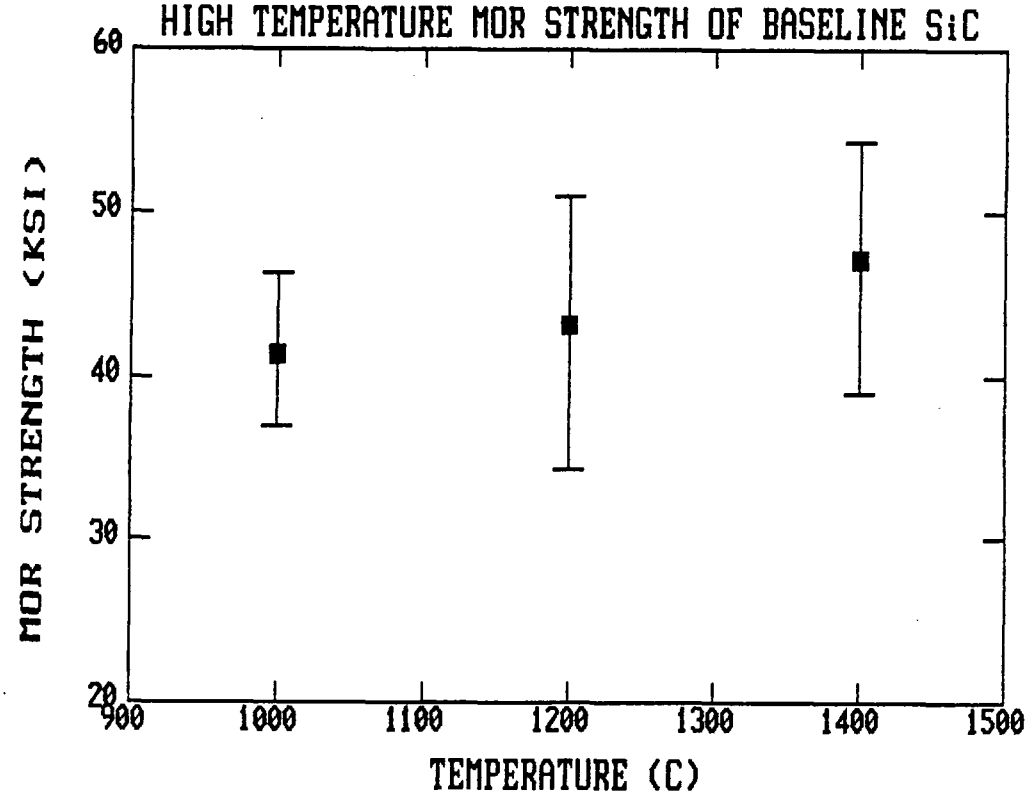
FLAW ORIGIN — SULFUR RICH



LT= 300 SECS

FRACTURE ORIGIN





TASK VII

OBJECTIVE:

CONTINUOUS THROUGHOUT THE PROGRAM

"ADVANCE THE STATE OF THE ART OF SiC TECHNOLOGY"

PROVIDE INPUT TO TASKS I AND II

WAYS TO IMPROVE THE STRENGTH OF A CERAMIC...

$$\sigma \propto K_I E / c^{1/2}$$

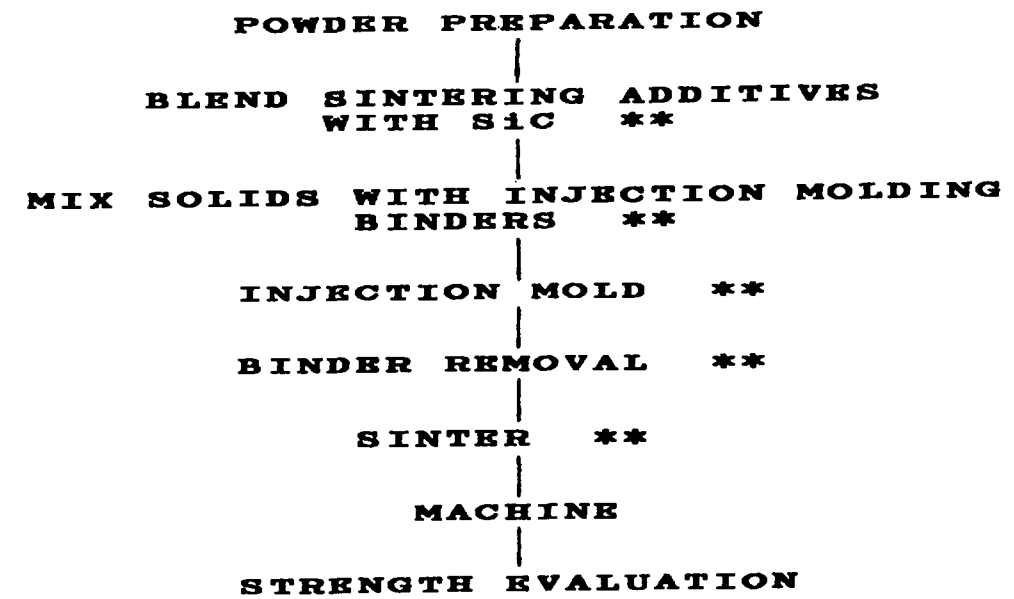
INCREASE THE FRACTURE TOUGHNESS (MICROSTRUCTURE)

INCREASE THE ELASTIC MODULUS (DENSITY) **

REDUCE THE FLAW SIZE **

** ADDRESSED IN TASK VII

INJECTION MOLDED SiC
PROCESS FLOW SHEET



** ADDRESSED IN TASK VII

DEVELOPMENT OF IMPROVED MIXING TECHNIQUES

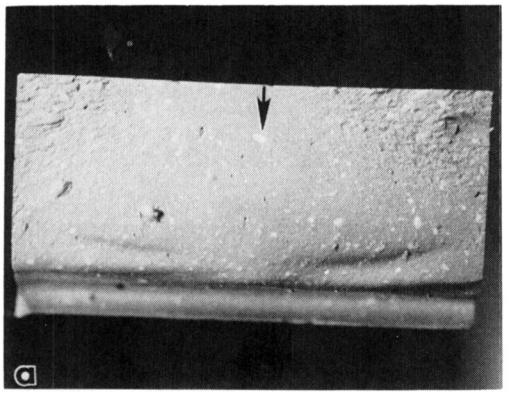
FRACTURE ORIGINS IDENTIFIED AS PROCESSING FLAWS

FLAWS IDENTIFIED AS AGGLOMERATES IN THE INJECTION MOLDING BATCH

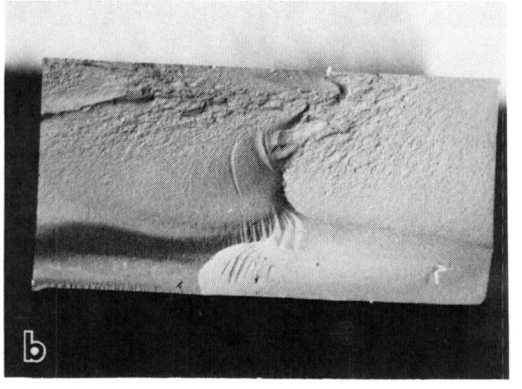
AGGLOMERATES WERE DETECTED IN THE "MIXING" STAGE OF THE PROCESS

"GREEN" INJECTION MOLDED TEST BARS

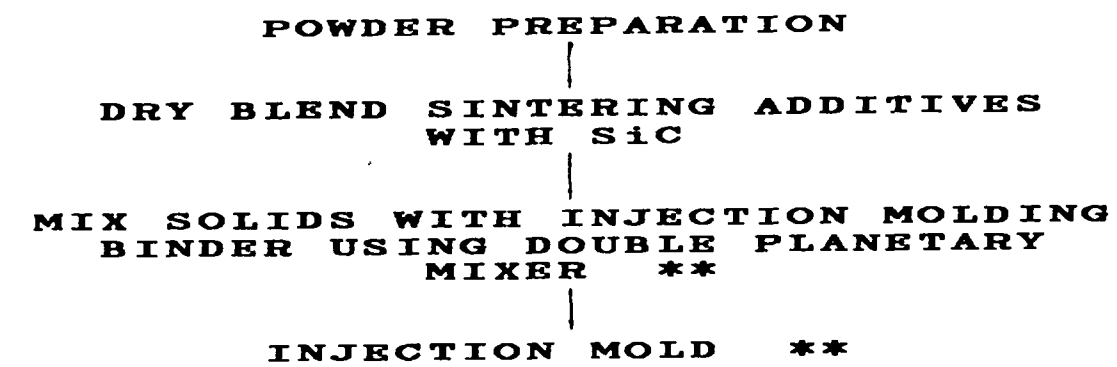
STRENGTH CONTROLLING AGGLOMERATES (UF POWDER)



NO AGGLOMERATES OBSERVED (SF POWDER)

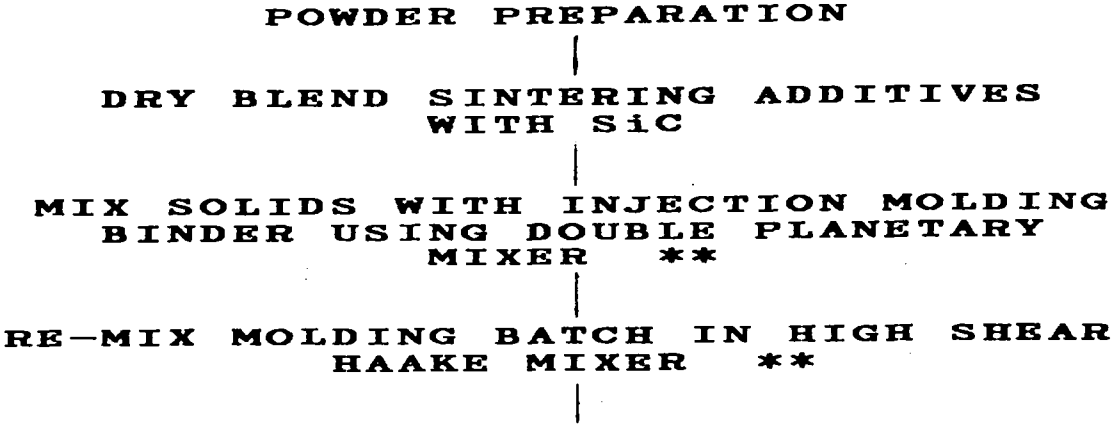


DRY MIXING PROCESS
(METHOD 1)



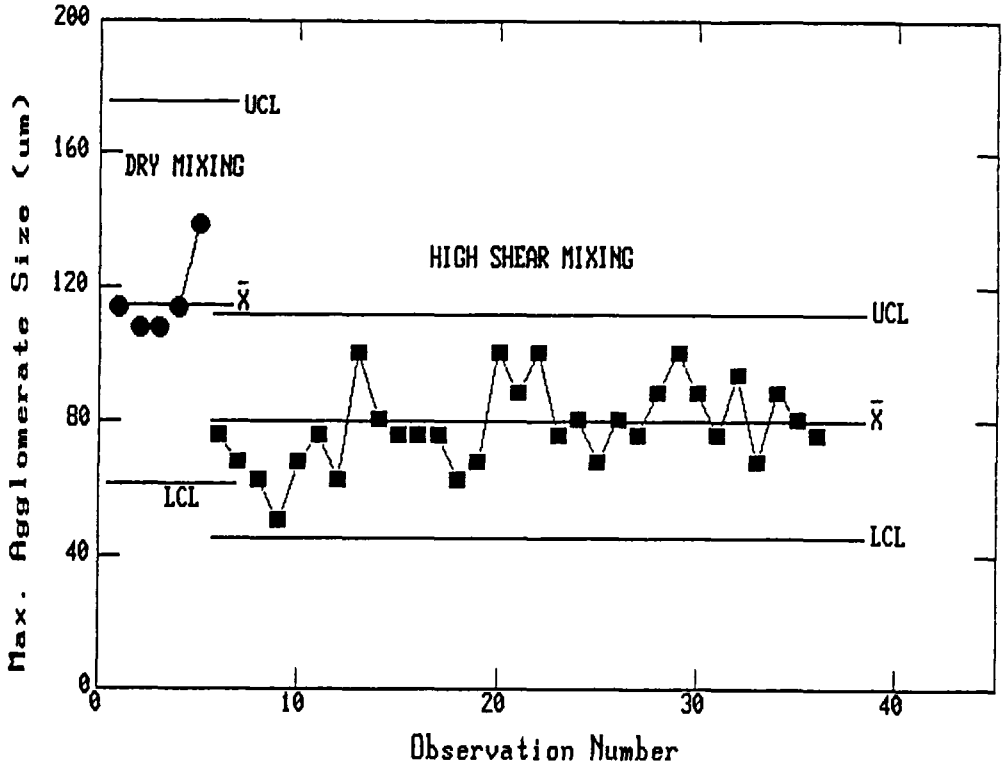
** AGGLOMERATES OBSERVED

DRY MIXING PROCESS
(METHOD 2)



** AGGLOMERATES OBSERVED

HIGH SHEAR MIXING WAS FOUND TO REDUCE THE AGGLOMERATE SIZE



FLUID MIXING WAS INVESTIGATED TO REDUCE AGGLOMERATE SIZE

FLUID MIXING PROCESS (METHOD 1)

POWDER PREPARATION

↓

FLUID BLEND SINTERING ADDITIVES WITH SiC

↓

FLUID BLEND SOLIDS WITH INJECTION MOLDING BINDERS (BINDERS DISSOLVED IN FLUID)

↓

REMOVE FLUID BY DRYING

↓

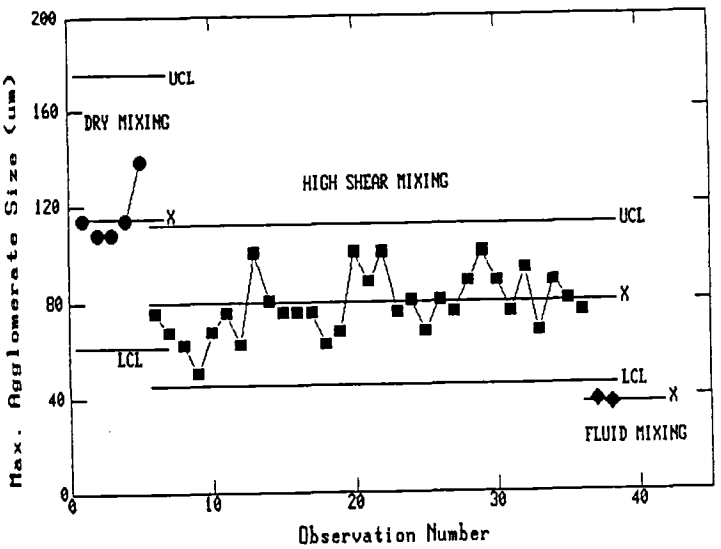
ADD ADDITIONAL WAX USING DOUBLE PLANETARY MIXER **

↓

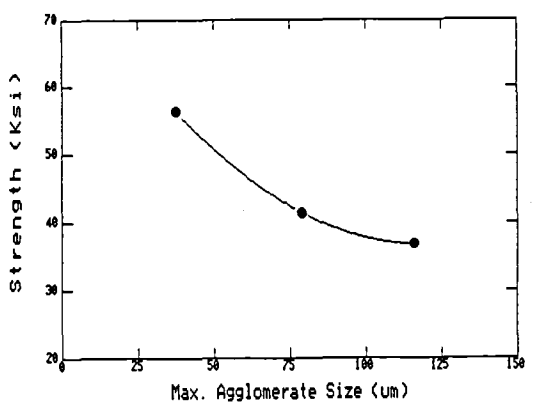
INJECTION MOLD **

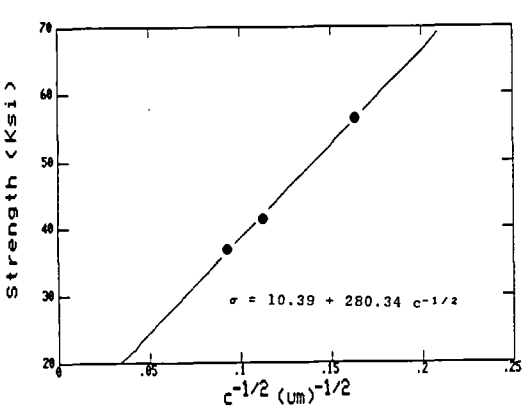
** AGGLOMERATES OBSERVED

FLUID MIXING WAS FOUND TO FURTHER REDUCE THE AGGLOMERATE SIZE



REGRESSION MODEL ILLUSTRATES THE RELATION BETWEEN STRENGTH AND AGGLOMERATE SIZE

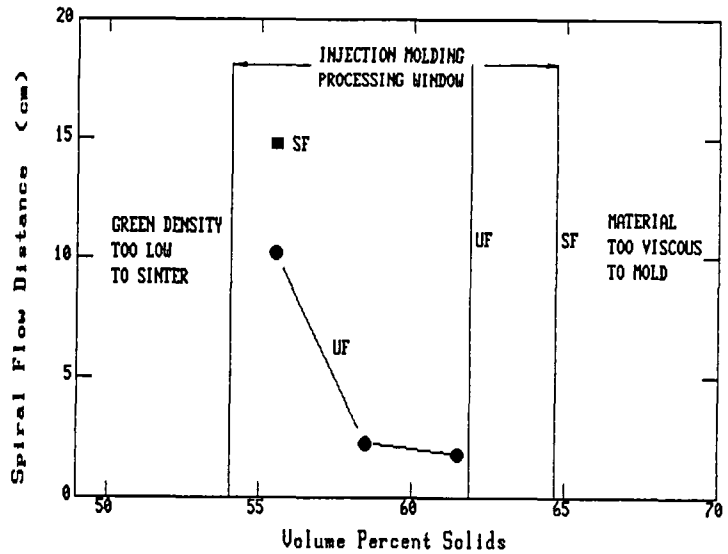




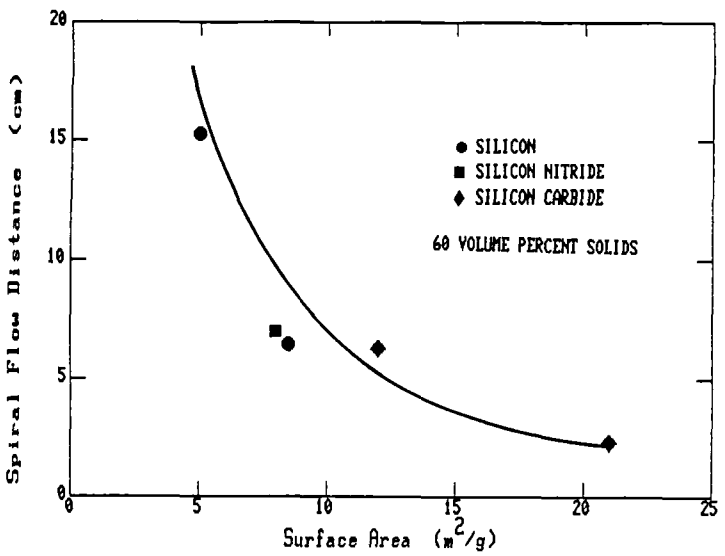
FLUID MIXING PROCESS WILL BE USED IN THE REMAINDER OF THE PROGRAM (TASK II)

INJECTION MOLDING

INJECTION MOLDING PROCESSING WINDOW WAS IDENTIFIED



INJECTION MOLDING BEHAVIOR OF ALL SILICON BASED CERAMIC POWDERS IS A FUNCTION OF SURFACE AREA



INJECTION MOLDING PROCESS YIELDS WERE IMPROVED THROUGH EQUIPMENT MODIFICATION

COMPOSITION: 12A — 60.0 VOL % SOLIDS

ORIGINAL SYSTEM:

332 BARS MOLDED
221 BARS VOID FREE

66.6 % YIELD

IMPROVED VACUUM SYSTEM:

24 BARS MOLDED
23 BARS VOID FREE

95.8 % YIELD

BINDER REMOVAL — SINTERING

CURRENT PROCESS USES
VACUUM FOR BINDER REMOVAL
VACUUM FOR SINTERING

VACUUM PROCESSING RESULTS IN CRACK FREE TEST BARS HAVING GOOD DENSITY

PROBLEMS ARE ANTICIPATED WITH VACUUM PROCESSING:

- CRACKING IN THICK CROSS SECTION COMPONENTS
- LOW DENSITY AREAS ON AS SINTERED SURFACES

EXPERIMENTS WERE INITIATED TO INVESTIGATE ALTERNATIVES TO VACUUM PROCESSING DURING BINDER REMOVAL AND SINTERING.

BINDER REMOVAL

2^2 EXPERIMENTAL DESIGN

VARIABLES:
HEATING RATE
PRESSURE

EXP.			PERCENT BINDER REMOVAL	VACUUM SINTERED DENSITY
1)	−	−	91.7	93.5
2)	+	−	91.4	93.6
3)	−	+	95.8	93.5
4)	+	+	96.4	93.8

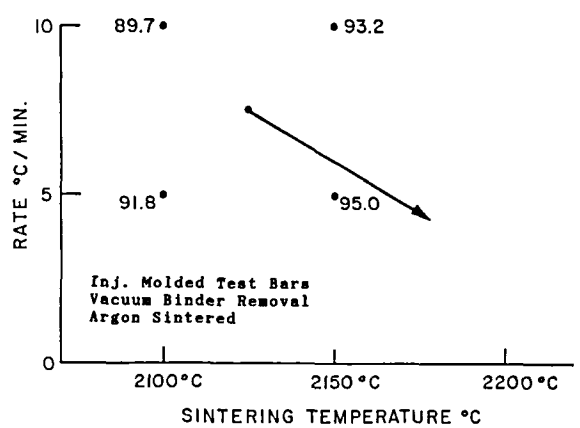
EXP. 1 USED FOR BASELINE PROCESSING

EXP. 3 OFFERS POTENTIAL FOR PROCESSING LARGE COMPONENTS

SINTERING

ARGON SINTERING POTENTIAL DEMONSTRATED

SINTERED DENSITY VS SINTERING VARIABLES



FUTURE PLANS

TASK II

$$\sigma \propto K_I E / c^{1/2}$$

FIRST ITERATION:

REDUCE PROCESSING FLAW SIZE (AGGLOMERATES)

SECOND ITERATION:

INCREASE DENSITY (ELASTIC MODULUS)

OPTIMIZE MICROSTRUCTURE (INCREASE FRACTURE TOUGHNESS)

FUTURE PLANS

TASK VII

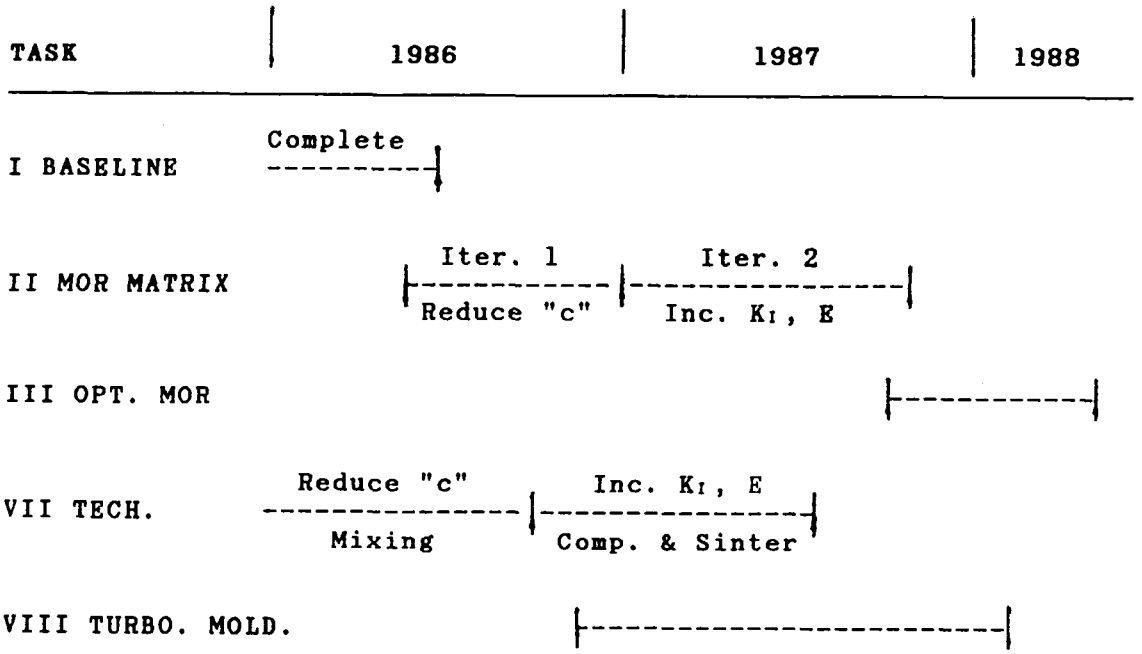
CONTINUE TO STUDY WAYS TO REDUCE AGGLOMERATE SIZE

CONTINUE TO INVESTIGATE BINDER REMOVAL TECHNIQUES

CONTINUE TO STUDY THE INTERRELATION BETWEEN BINDER REMOVAL AND SINTERING

INITIATE WORK TO INCREASE SINTERED DENSITY AND IMPROVE SINTERED MICROSTRUCTURE

PROGRAM TIMING CHART
PHASE I



STRENGTH OPTIMIZATION OF α-SiC BY IMPROVED PROCESSING

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Silicon carbide is of great interest for structural use in aircraft and automobile engines. This ceramic combines high thermal conductivity and low coefficient of thermal expansion, and consequently has good thermal shock resistance. However, like other ceramics, silicon carbide shows strength variability due to processing flaws such as large voids, shrinkage cracks, inclusions, etc. Agglomerates in the starting powder seem to be the predominant cause for such defects. Improved processing techniques such as slurry pressing and hot isostatic pressing were employed to minimize these defects and to improve strength and reliability in the fabricated material. For this purpose 2-inch diameter discs were fabricated by various consolidation techniques. These include: (1) dry pressing and sintering, (2) slurry pressing and sintering, and (3) slurry pressing and HIPing. High density (>96 percent of theoretical) was produced by sintering at 2150 - 2200 °C. By contrast, a much lower temperature (1850-1900 °C) was required by HIPing to achieve high final density specimens. Dry pressing and sintering yielded an average flexure strength (4-point bend) of 350 MPa (50 ksi), while slurry pressing and sintering produced an average strength of 430 MPa (62 ksi), a 30 percent improvement in strength. Further, slurry pressing and HIPing yielded an average strength of 580 MPa (84 ksi). This strength value is 60 percent higher than the dry-pressed/sintered strength, and 30 percent higher than the slurry-pressed/sintered strength. The HIP silicon carbide exhibited an ultrafine grained microstructure (0.3-3 μm) as compared to 1-30 μm produced by sintering. Process related defects such as large isolated voids, shrinkage cracks, etc. were not observed in HIPed silicon carbide.

TABLE 1 ANALYSIS OF AS-RECEIVED α - SiC POWDERS

	IMPURITY ANALYSIS (PPM)		
	TYPE 1	TYPE 2	TYPE 3
ELEMENT	α - SiC (100%)	α - SiC (B, C)	α - SiC (Al, C)
Al	50	140	1.2*
Ca	70	40	20
Fe	10	10	40
Ti	20	30	50
V	20	20	40
B	–	0.60*	--
FREE C	1.66*	7.31*	6.10*
SURFACE AREA (BET) m^2/gm	31.47	4.19	11.38

*WT PERCENT

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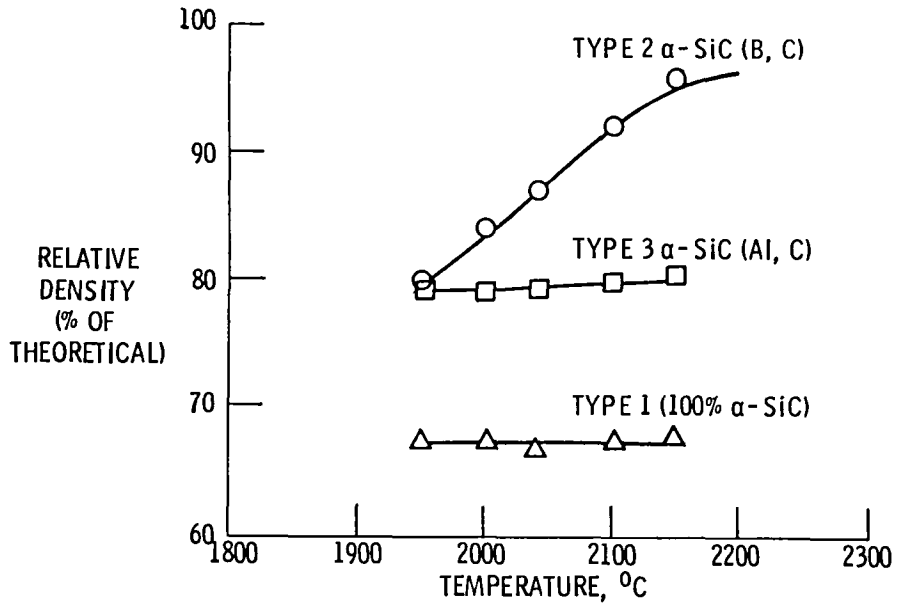
RELATIVE DENSITY OF THREE TYPES OF STARCK α-SiC POWDER SINTERED FOR 30 min AT DIFFERENT TEMPERATURES



V-1270

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PROCESSING AND PROPERTIES OF TYPE 2 (AS-RECEIVED) α - SiC (B, C) MATERIAL

α - SiC TYPE	SINTERED TEMPERATURE, °C	TIME, min	DENSITY, g/cm^3	MOR/TEST TEMPERATURE,	NUMBER OF SPECIMEN	MEAN MOR/δ-D., MPa	WEIBULL/R^2, m
2	2150	30	95	RT	23	353/	11/95
2	2150	60	96	RT	28	306/32	12/97
2	2200	30	97	RT	30	404/40	12/89
2	2150	30	95	1370	20	312/	7/97
2	2150	60	96	1370	24	265/32	10/94
2	2200	30	97	1370	30	316/53	7/80

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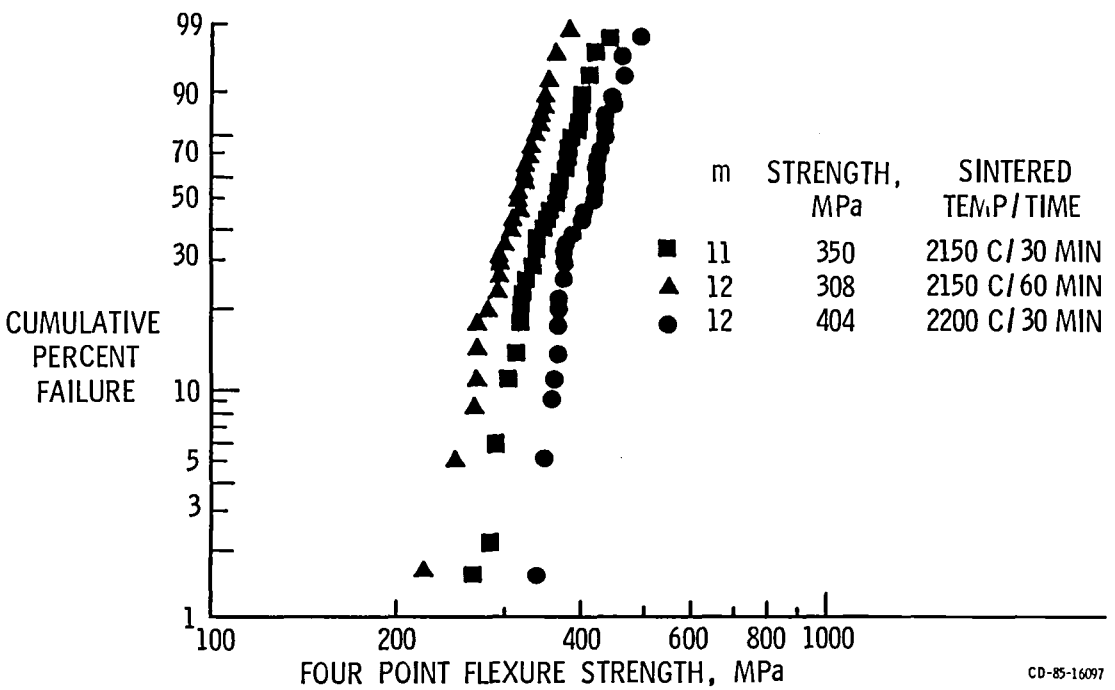
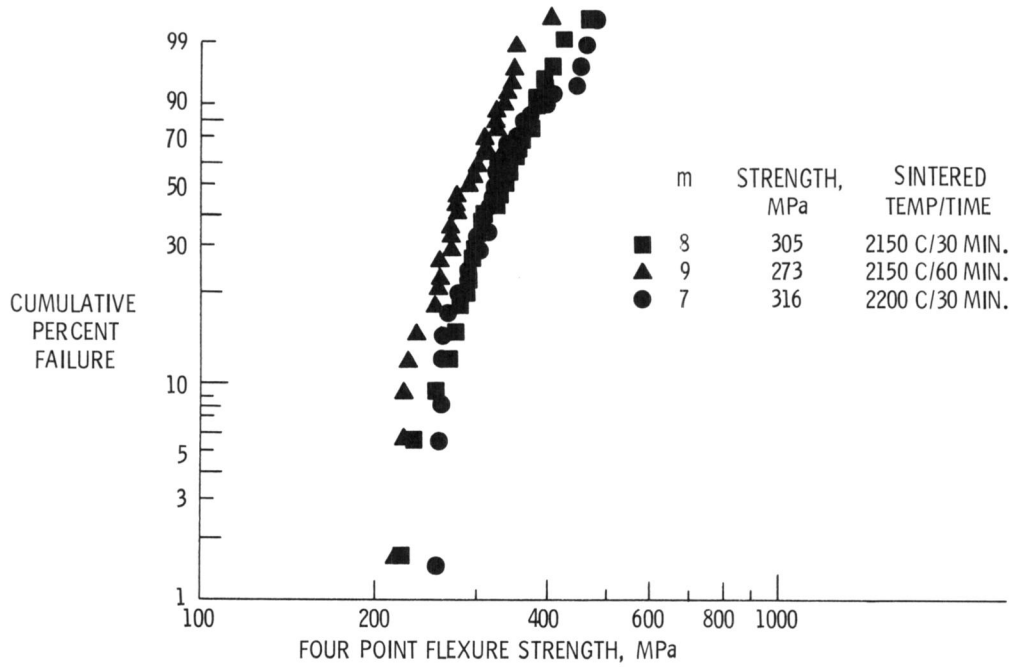
WEIBULL PROBABILITY CHART FOR ROOM TEMPERATURE
FRACTURE OF STARCK TYPE 2 α - SiC (B, C)



WEIBULL PROBABILITY CHART FOR 1370° C FRACTURE OF STARCK TYPE 2 α - SiC (B, C)



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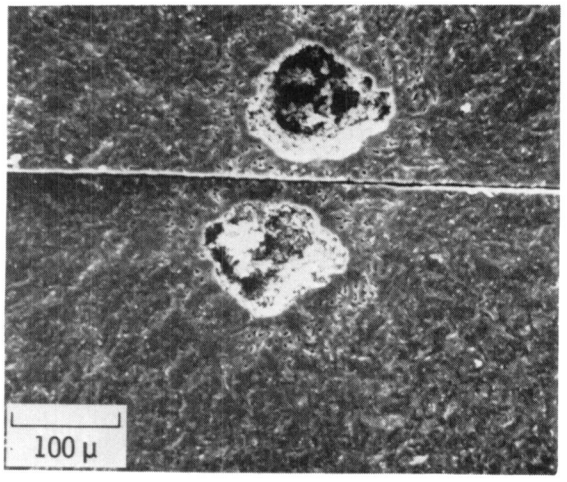
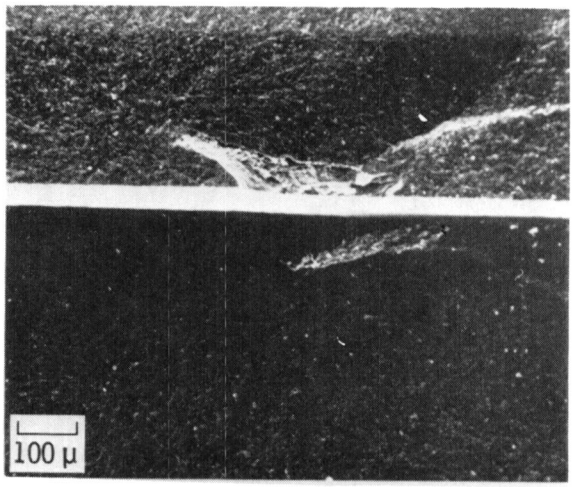
ROOM TEMPERATURE FRACTURE OF DRY-PRESSED/SINTERED α-SiC



σ_f – 227 MPa



σ_f – 225 MPa

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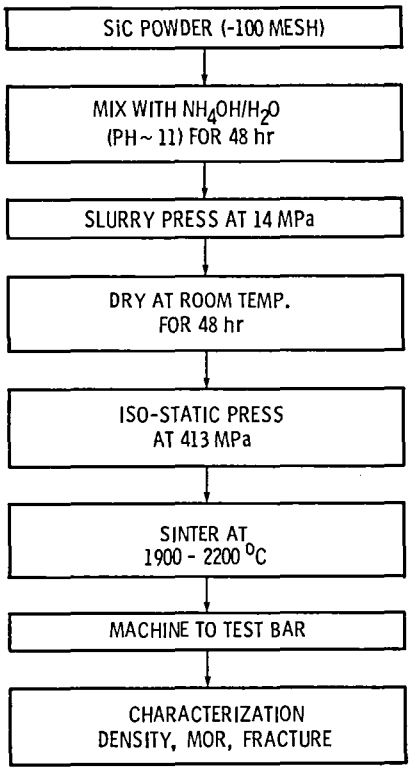
SLURRY-PRESSING FLOW DIAGRAM



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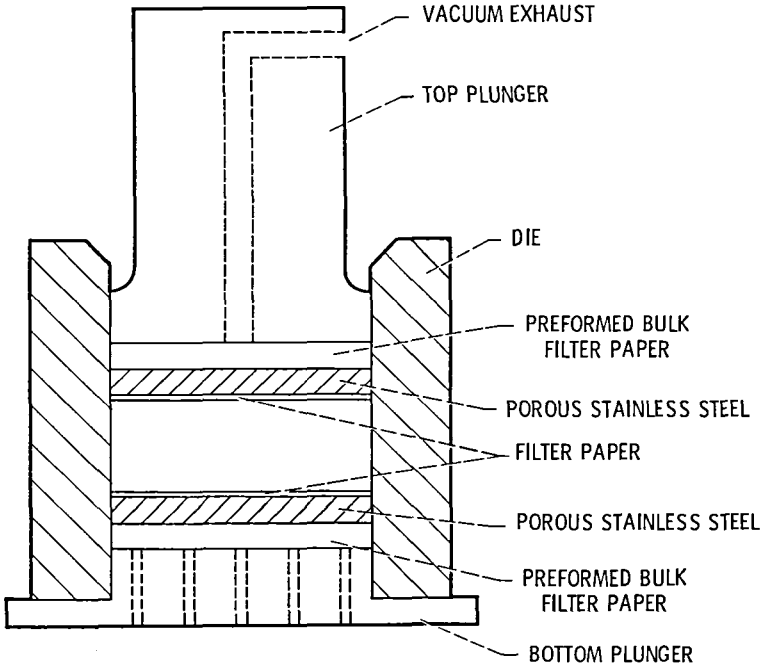
SCHEMATIC OF SLURRY PRESSING APPARATUS



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PROPERTIES OF SINTERED VS HOT ISOSTATIC PRESSED α - SiC

α - SiC TYPE	PROCESSING METHOD	DENSIFICATION TEMPERATURE, ^{O}C	TIME, min	DENSITY (% OF THEORETICAL)	MEAN MOR/6-D MPa	NO. OF SPECIMEN	WEIBULL/R^2 m
2	DRY PRESS/ SINTERED	2200	30	97.4	342± 52.8 (49.6±5.7 ksi)	30	8
2	SLURRY PRESS/ SINTERED	2200	30	96.5	416± 53.3 (60.3± 7.7 ksi)	22	9.3
2	SLURRY PRESS/ HIPed	1900	30	95.3	580± 77	15	8.8
2	SLURRY PRESS/ HIPed	1800	30	80.5	N.D.	8	N.D.

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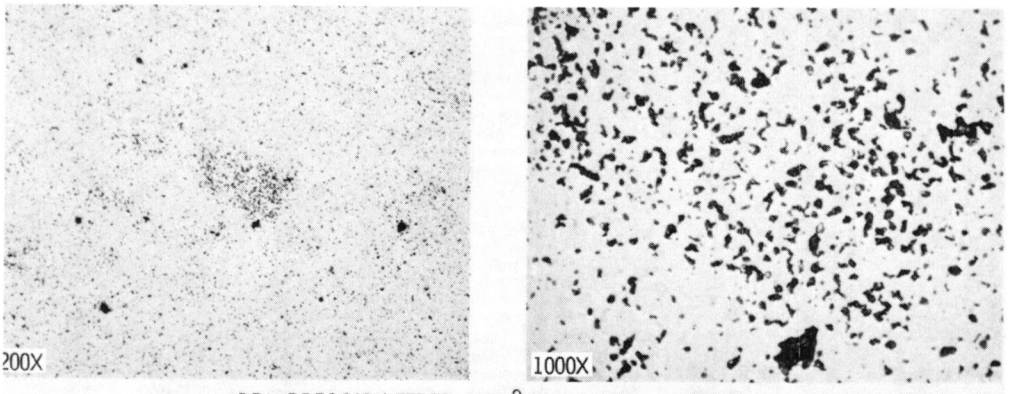
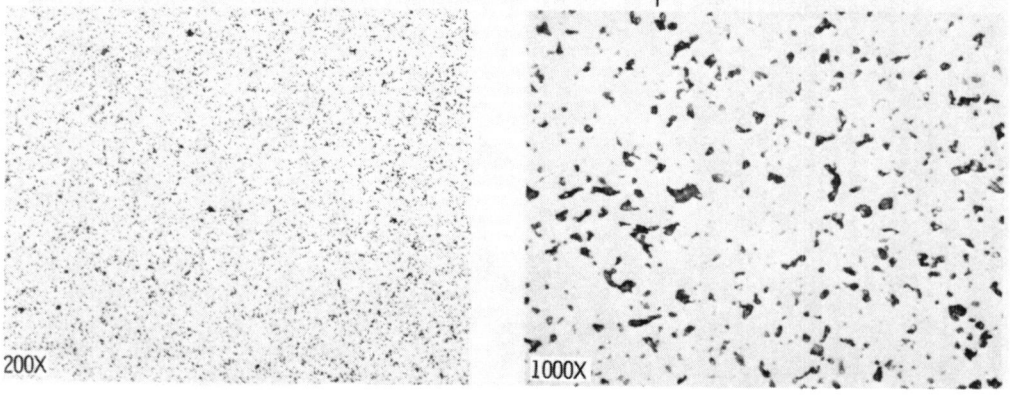
EFFECT OF DRY PRESSING VS SLURRY PRESSING ON SINTERED MICROSTRUCTURES OF α-SiC



DRY PRESS/SINTERED 2200 ^{O}C/1/2 hr/RT σ_f - 345 MPa



SLURRY PRESS/SINTERED 2200 ^{O}C/1/2 hr/RT σ−480 MPa

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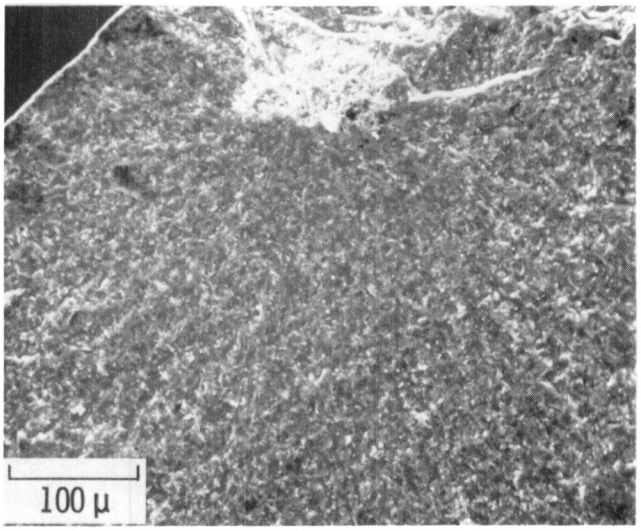
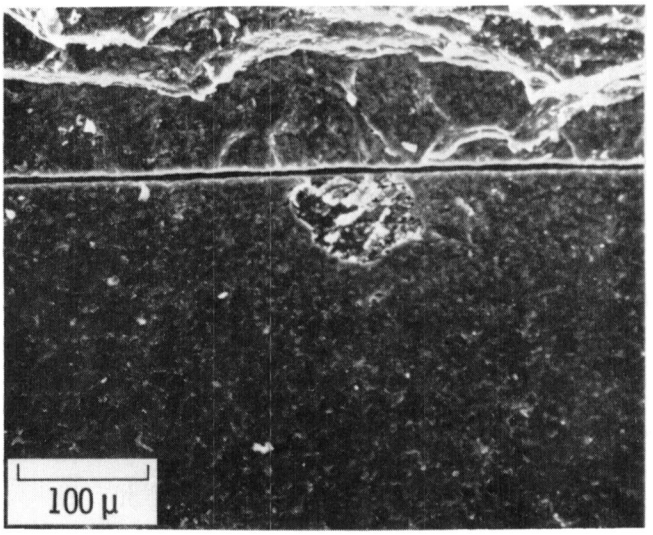
ROOM TEMPERATURE FRACTURE OF SLURRY-PRESSED/SINTERED α-SiC



σ_f – 340 MPa



σ_f – 260 MPa

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HIPing OF STRUCTURAL CERAMICS

ADVANTAGES:

HOT ISOSTATIC PRESSING (HIPing) OF STRUCTURAL CERAMICS, e.g., Si_3N_4 AND SiC.

- o ENHANCES DENSITY (APPROACHES TD)
- o IMPROVES MICROSTRUCTURE
- o SIGNIFICANTLY INCREASES STRENGTH
- o IMPROVES RELIABILITY

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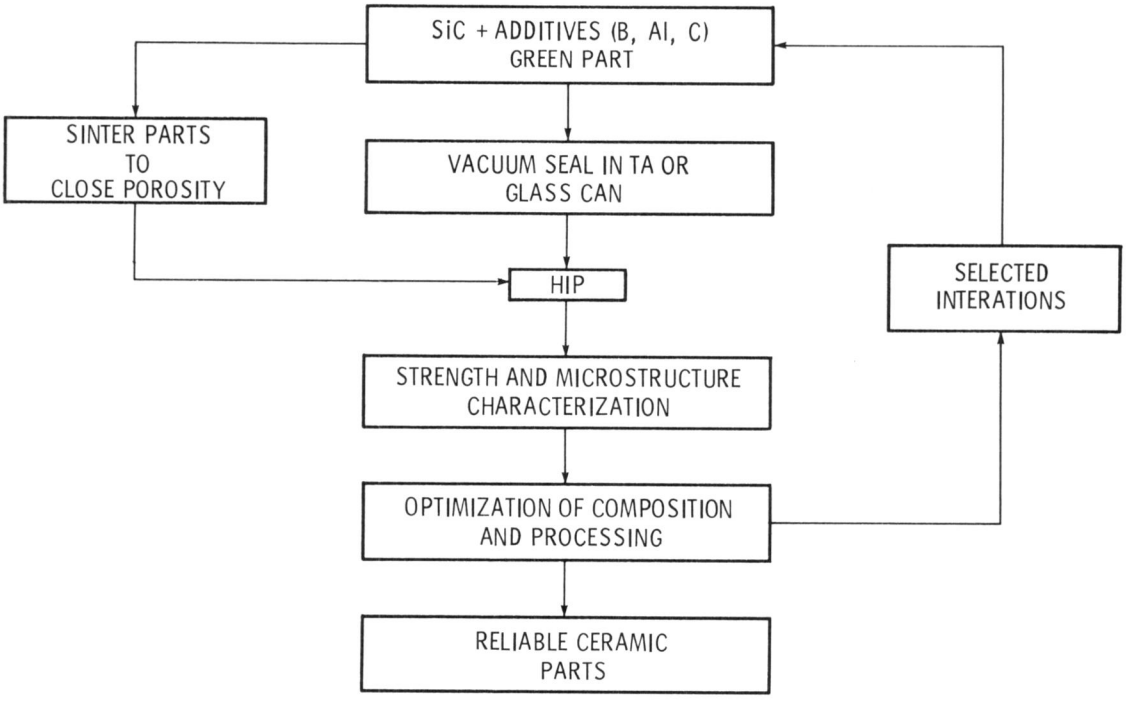
HOT ISOSTATIC PRESSING - GENERAL FLOW CHART



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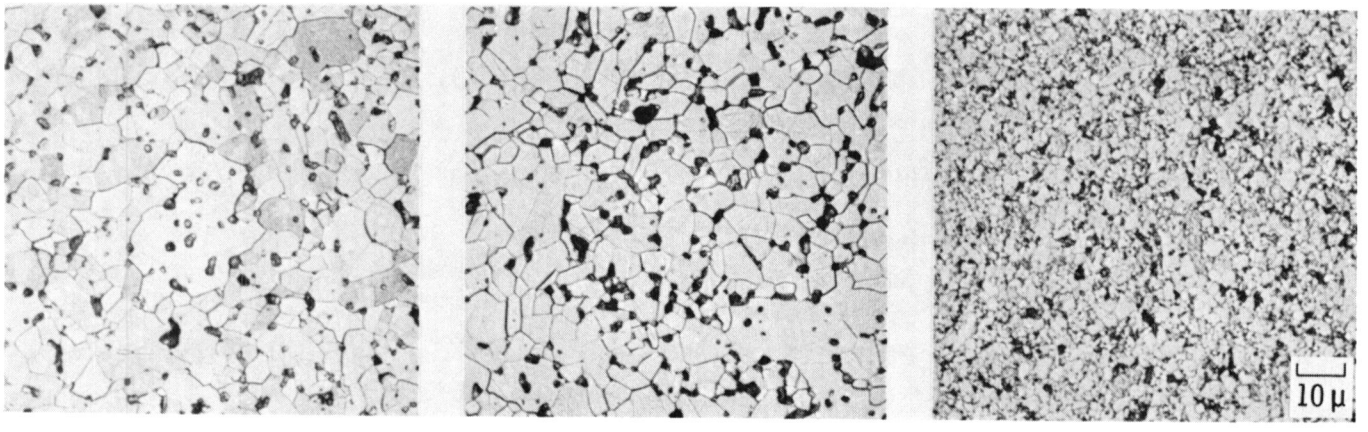
MICROSTRUCTURE DEVELOPMENT IN SINTERED AND HOT ISOSTATIC PRESSED α-SiC

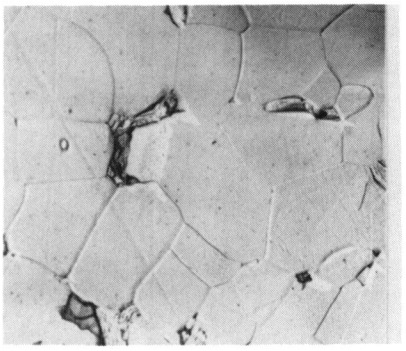


DRY-PRESSED/SINTERED
2200 C / 1/2 hr

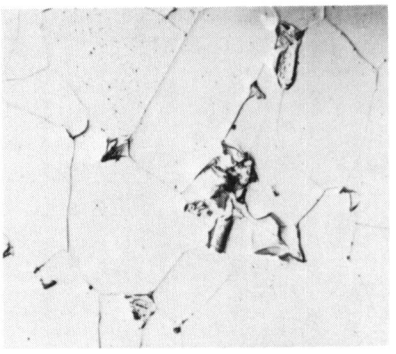
SLURRY-PRESSED/SINTERED
2200 C/ 1/2 hr

SLURRY-PRESSED/HIPed
1900 C / 1/2 hr

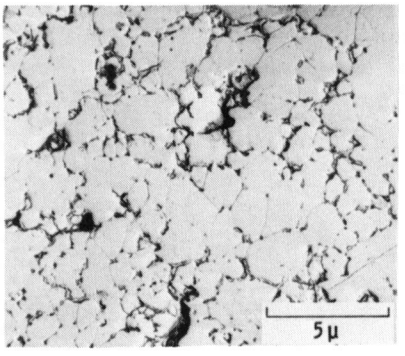
REPLICA PHOTOMICROGRAPHS OF SINTERED AND HOT ISOSTATIC PRESSED α-SiC



DRY-PRESSED/SINTERED



SLURRY-PRESSED/SINTERED



SLURRY-PRESSED/HIPed

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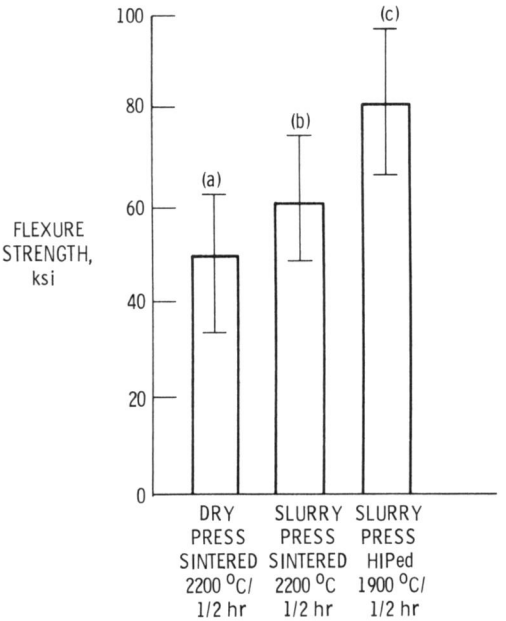
ROOM TEMPERATURE FLEXURE STRENGTH OF SINTERED VS HIPed SILICON CARBIDE



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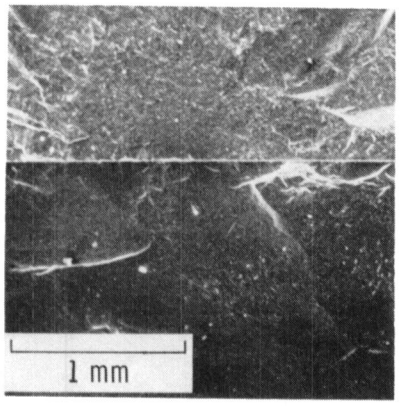
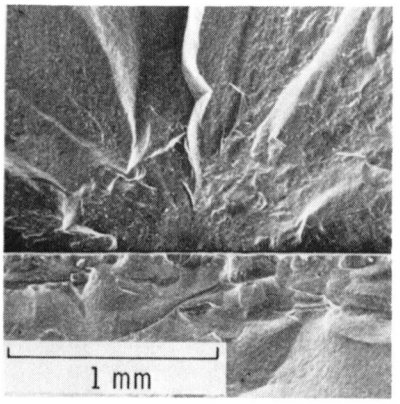
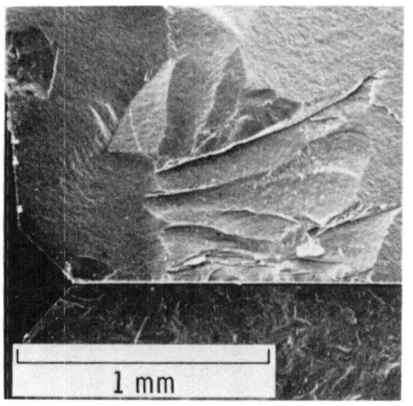
ROOM TEMPERATURE FRACTURE OF HOT ISOSTATIC PRESSED α-SiC



σ_f – 445 MPa



σ_f – 480 MPa



σ_f – 530 MPa

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CONCLUSIONS

- DRY PRESSING / SINTERING OF STARCK ALPHA SILICON CARBIDE PRODUCED HIGH DENSITY BODIES WITH AN AVERAGE FLEXURE STRENGTH (4-POINT BEND) OF 350 MPa (50 ksi).
- IN CONTRAST, SLURRY PRESSING / SINTERING PRODUCED AN AVERAGE STRENGTH OF 430 MPa (62 ksi), A 30% IMPROVEMENT IN STRENGTH.
- FURTHER, SLURRY PRESSING / HOT ISOSTATIC PRESSING (HIPing) PRODUCED HIGH DENSITY BODIES AT 1850 - 1900 ^{o}C, WITH AN AVERAGE STRENGTH OF 580 MPa (84 ksi). THIS STRENGTH VALUE IS 60% HIGHER THAN THE DRY-PRESSED / SINTERED STRENGTH, AND 30% HIGHER THAN THE SLURRY-PRESSED / SINTERED STRENGTH.
- THE SLURRY-PRESSED / HIPed MATERIAL EXHIBITED AN ULTRAFINE GRAINED (0.3 - 3 μm) MICROSTRUCTURE AS COMPARED TO 1 - 30 μm PRODUCED BY SINTERING.
- PROCESS RELATED DEFECTS SUCH AS LARGE VOIDS, AND SHRINKAGE CRACKS WERE NOT OBSERVED IN HIPed SILICON CARBIDE.

IMPROVED SILICON NITRIDE FOR ADVANCED HEAT ENGINES

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and

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Phoenix, AZ

Silicon nitride is a high temperature material currently under consideration for heat engine and other applications. This presentation describes the progress made in the first 1-1/2 years of a NASA funded, 5 year program on improved Si_3N_4. The objective of this program is to improve the net shape fabrication technology of Si_3N_4 by injection molding. This is to be accomplished by optimizing the process through a series of statistically designed matrix experiments. To provide input to the matrix experiments, a wide range of alternate materials and processing parameters were investigated throughout the whole program.

The improvement in the processing is to be demonstrated by a 20 percent increase in strength and a 100 percent increase in the Weibull modulus over that of the ACC baseline material. A full characterization of the baseline material/process was completed. The room temperature MOR and Weibull modulus of the as-processed test bars were established as 79.3 ksi and 7.9, respectively. In the first iteration of the MOR matrix experiments, a material with a room temperature MOR of 97 ksi and a Weibull modulus of 14 has been developed.

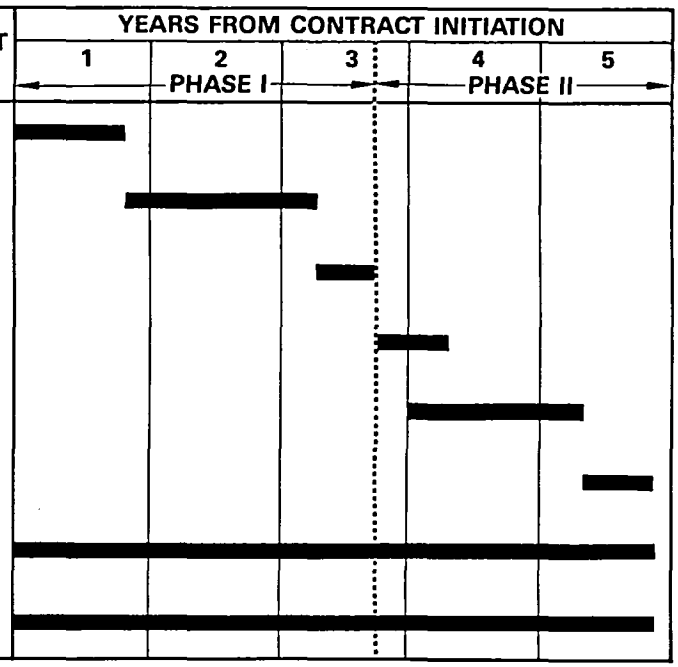
Material properties were found to be highly dependent on each step of the process. Several important parameters identified thus far are the starting raw materials, sinter/HIP cycle, powder bed, mixing methods, and sintering aid levels.

OBJECTIVES

- DEVELOP FABRICATION TECHNOLOGY BASE
- INCREASE THE AS PROCESSED TEST BAR STRENGTH BY 20% (RT THRU 2550°F)
- INCREASE WEIBULL MODULUS BY 100%
- ACHIEVE INJECTION MOLDING CAPABILITY FOR LARGE COMPONENTS

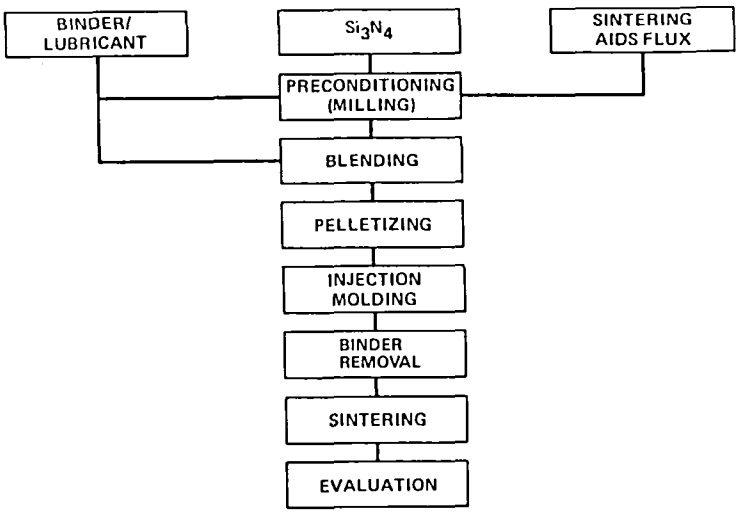
NASA WORK STATEMENT: SCHEDULE AND EFFORT

TASK NO.	DESCRIPTION	PERCENT EFFORT
I.	BASELINE CHARACTERIZATION	5
II.	MOR MATRIX	25
III.	OPTIMIZED MOR	5
IV.	BASELINE LARGE SHAPE	10
V.	LARGE SHAPE MATRIX	25
VI.	OPTIMIZED LARGE SHAPE	10
VII.	MATERIAL/PROCESS IMPROVEMENT	15
VIII.	REPORTS/PROJECT MANAGEMENT	5

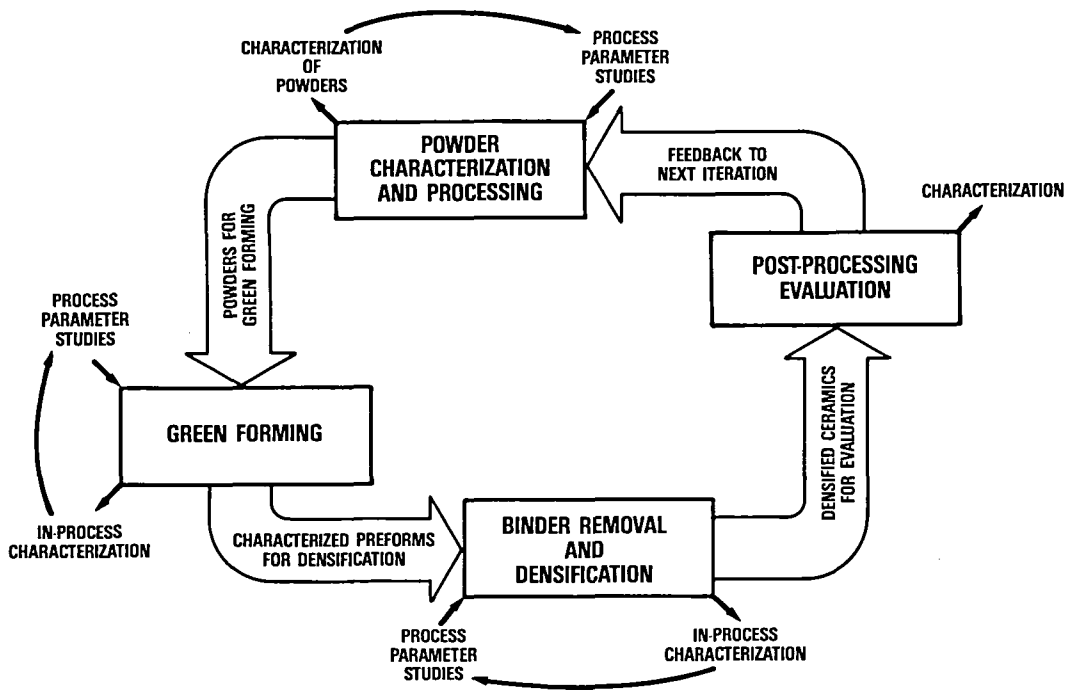


SPA 8596-74A

INJECTION MOLDING PROCESS



ITERATIVE APPROACH FOR IMPROVING CERAMIC MATERIAL PROPERTIES AND PROCESS CONTROLS



SPA 8777-5

PROCESSING VARIABLES

STARTING POWDER

- ALTERNATE Si_3N_4
- ALTERNATE ADDITIVES
- LOT VARIATIONS

TOOLING

- GATE SIZE
- GATE ORIENTATION
- SEPARATION DESIGN
- TEST BARS PER SHOT

INJECTION MOLDING

- MACHINE
- TEMPERATURES
- PRESSURE
- RAM SPEED
- VACUUM

COMPOSITION

- % $A1_2O_3$, Y_2O_3
- ZrO_2
- Y_2O_3-SiO_2

ADDITIVES

- ALTERNATE BINDERS
- % BINDER
- PLASTICIZER
- WETTING AGENT
- LUBRICANT
- DISPERSANT
- ACID-BASE CONTROL

DEWAX

- TEMPERATURE
- PRESSURE
- CYCLE
- APPROACH
- TIME
- EQUIPMENT
- CYCLE

POWDER PROCESSING

- ALTERNATE MILLING
- CLASSIFICATION
- ELUTRIATION/WASHING
- MILLING AIDS
- TIME

MIXING

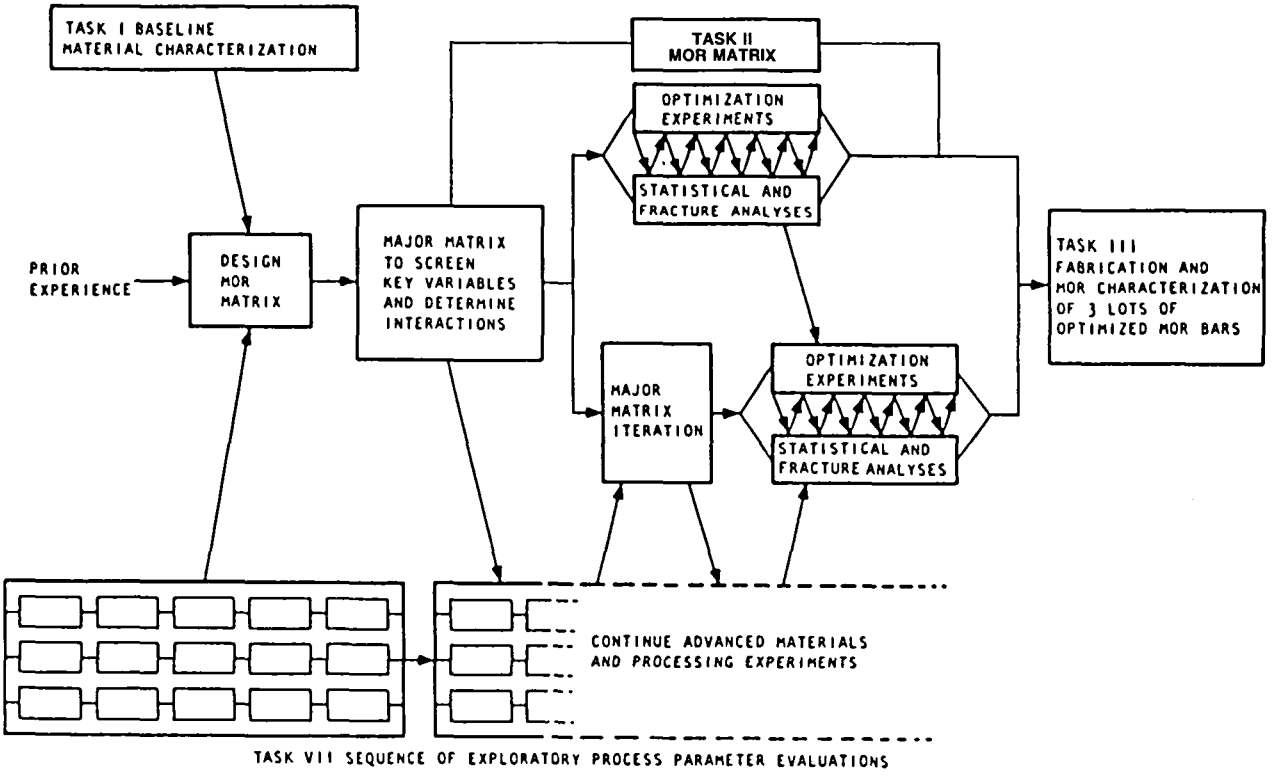
- MIXER
- TIME
- TEMPERATURE
- SHEAR RATE
- SOLVENT
- VACUUM

SINTERING

- TIME
- TEMPERATURE
- OVERPRESSURE
- CYCLE
- EQUIPMENT
- FIXTURING

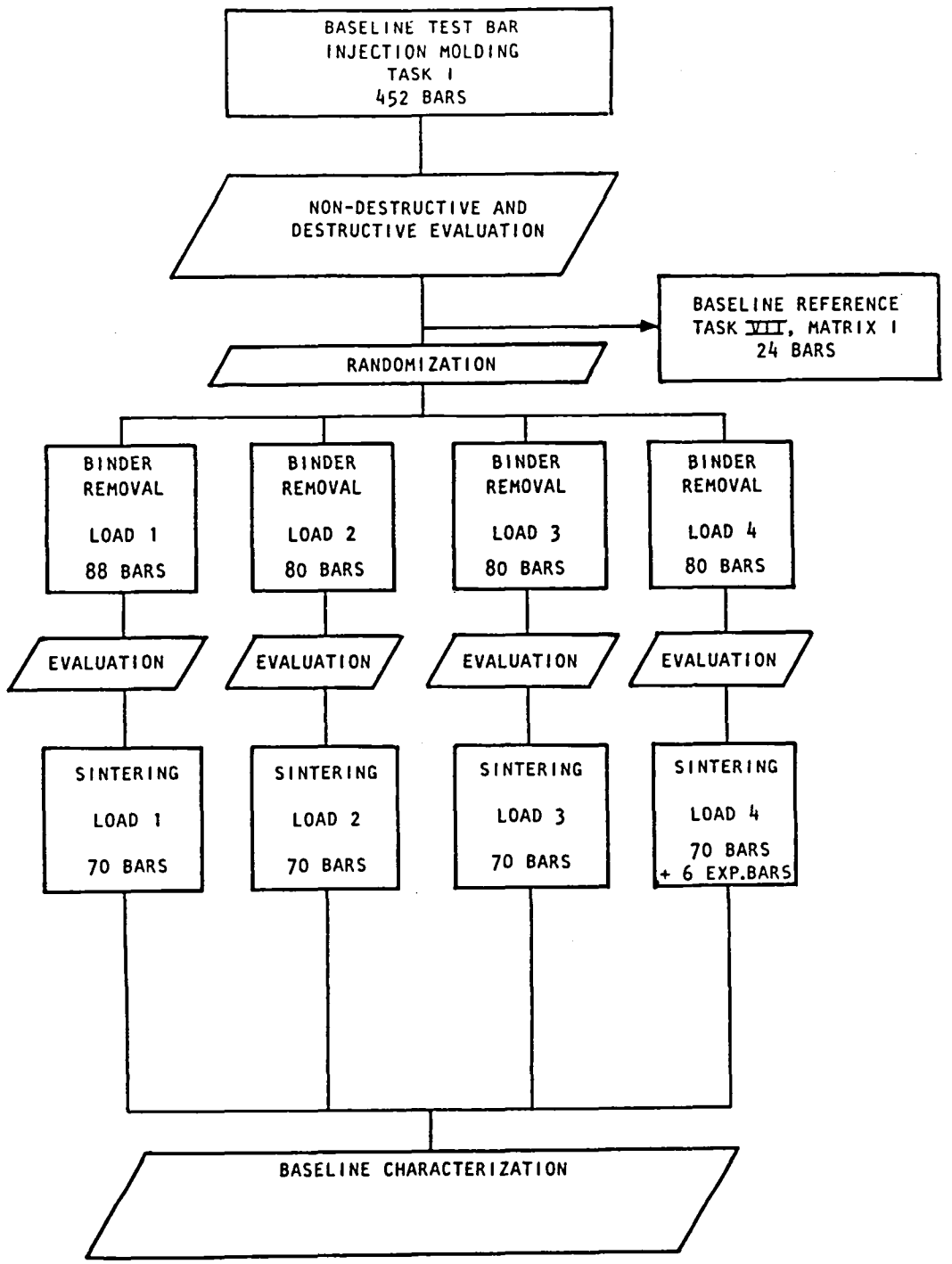
SPA 8596-191A

PHASE I DIRECTED TOWARDS TEST BARS



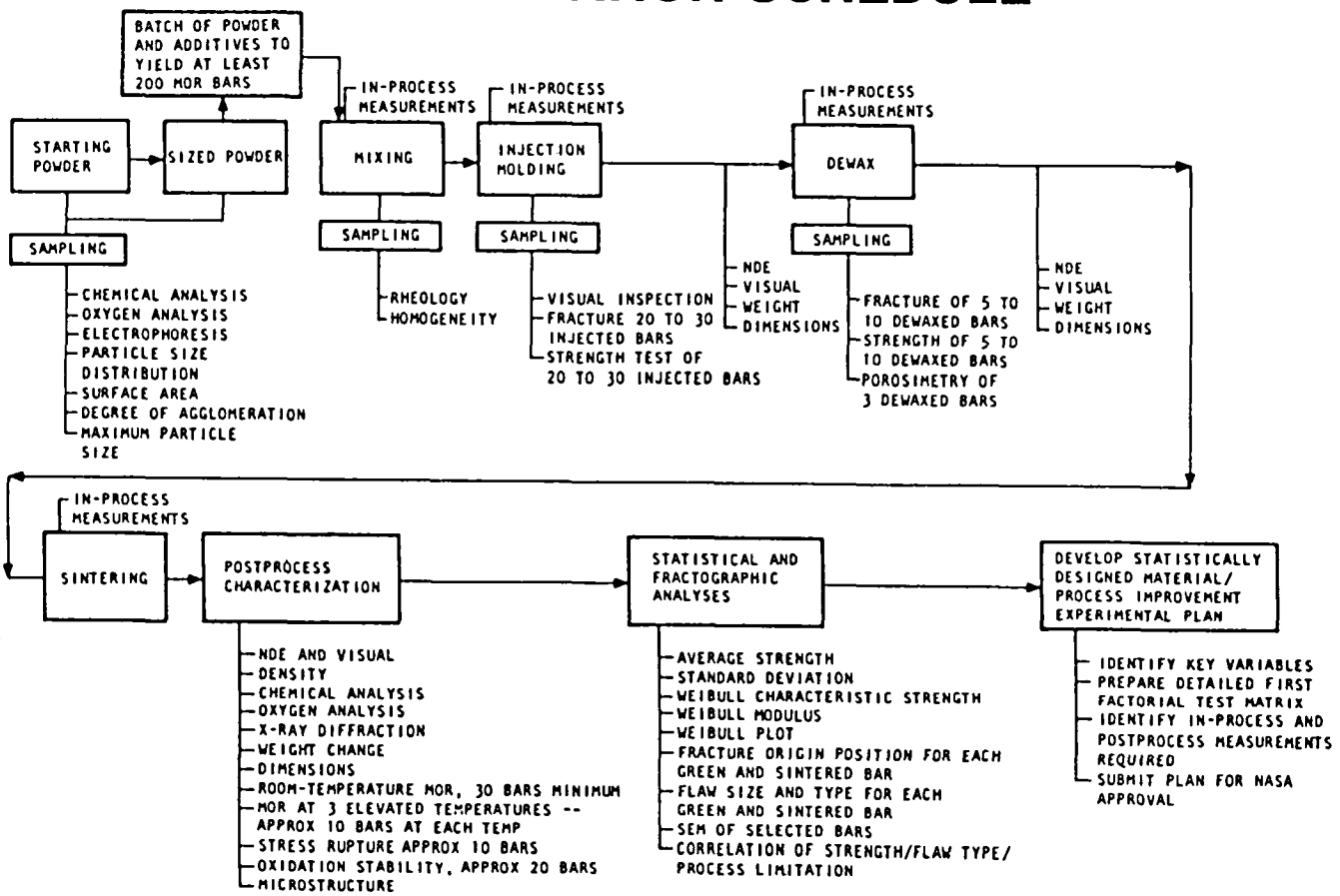
SPA 8596-79C

NASA IMPROVED Si_3N_4



SPA 8597-4B

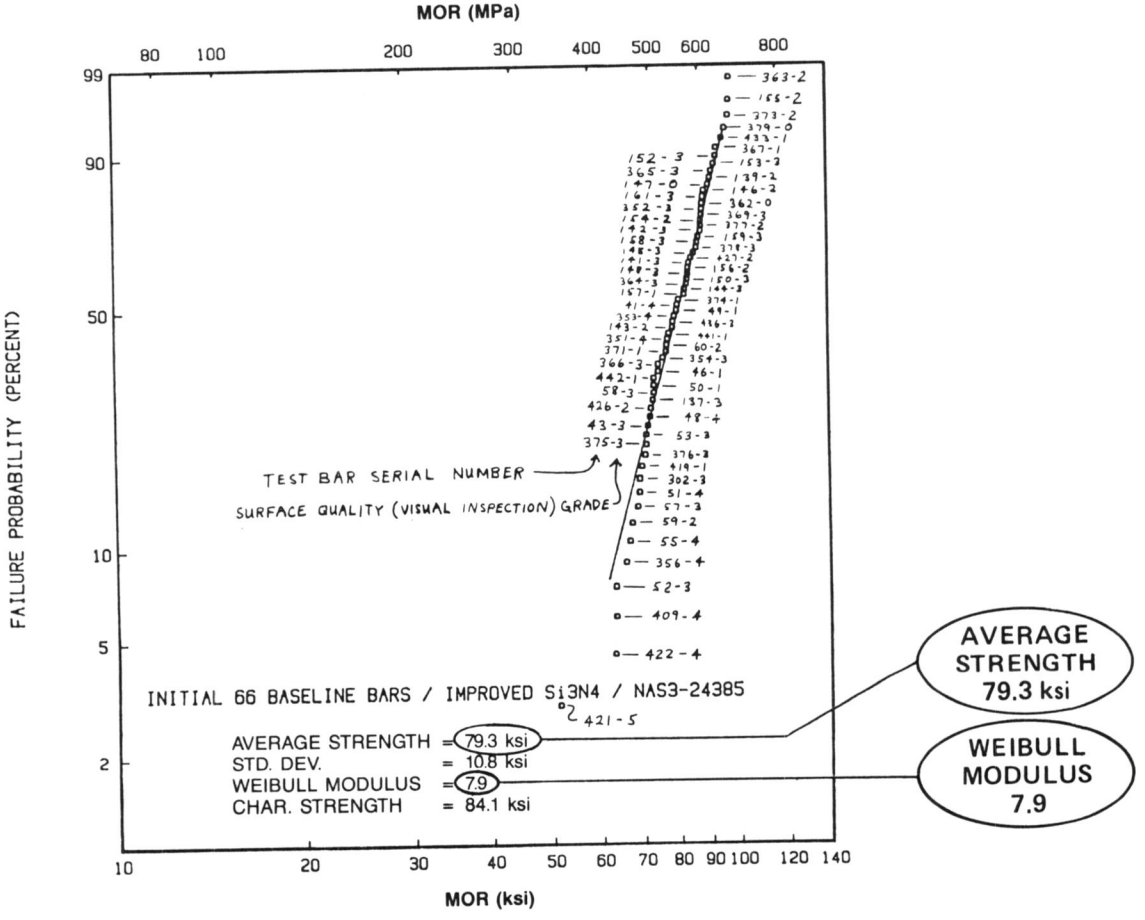
NASA IMPROVED Si_3N_4
TASK I PROCESS FLOW CHART AND CHARACTERIZATION SCHEDULE



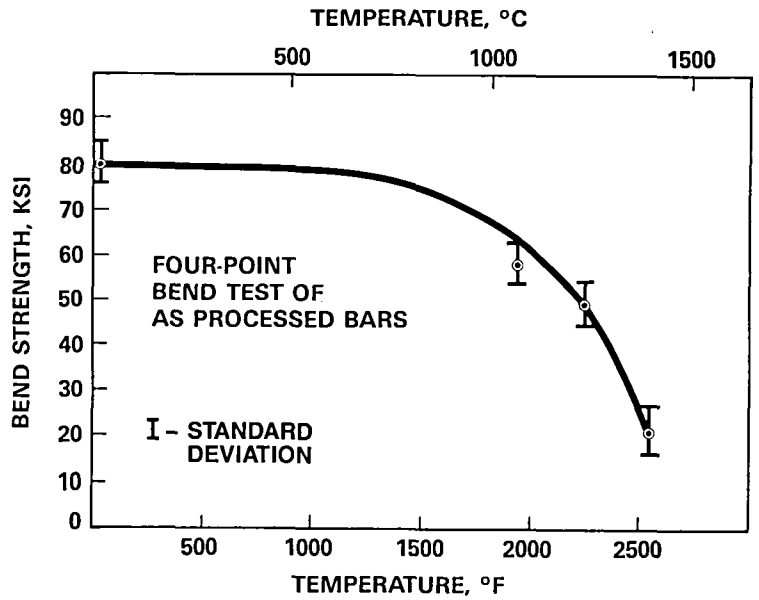
SPA 8596-80A

TEST BAR SINTERING SUPPORT

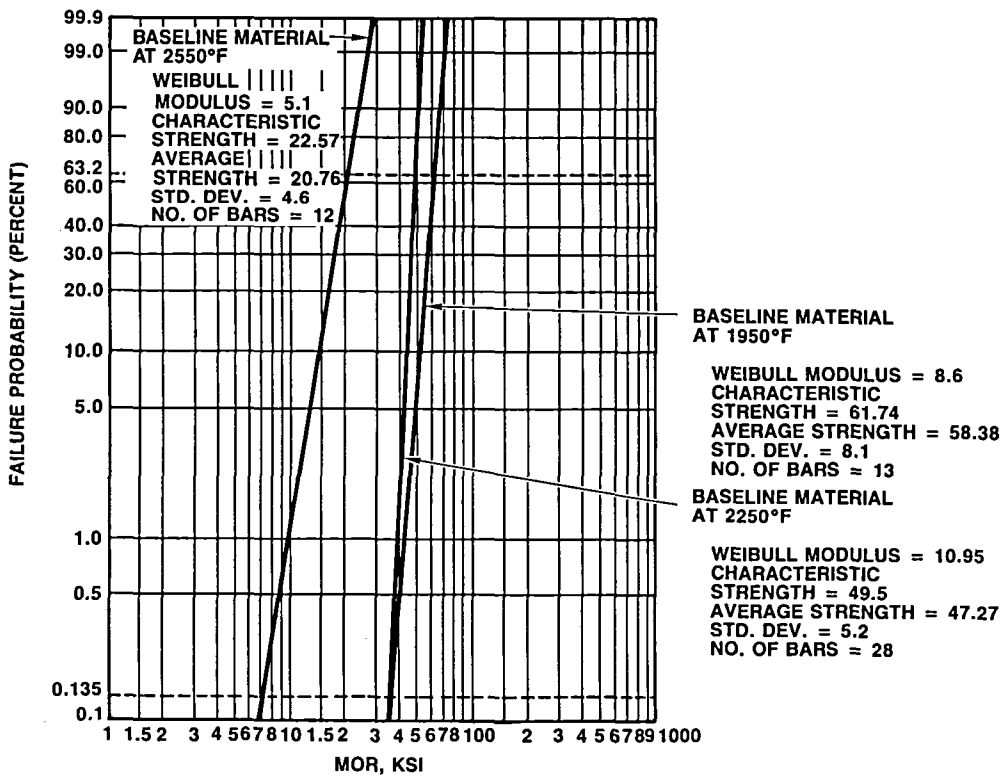
WEIBULL ANALYSIS OF BASELINE ROOM TEMPERATURE DATA



BASELINE STRENGTH



WEIBULL DISTRIBUTION FOR HIGH TEMPERATURE DATA



SPA 8794-10A

BASELINE STRESS RUPTURE

PRELIMINARY TEST CONDITIONS

1800°F	2200°F	2500°F
10 KSI — 24 HR	10 KSI — 24 HR	10 KSI — 9 HR, 42 MIN
20 KSI — 24 HR	20 KSI — 24 HR	
30 KSI — 24 HR	30 KSI — 24 HR	
40 KSI — 1 MIN	40 KSI — 24 HR	
	50 KSI — 0	

FINAL TEST RESULTS

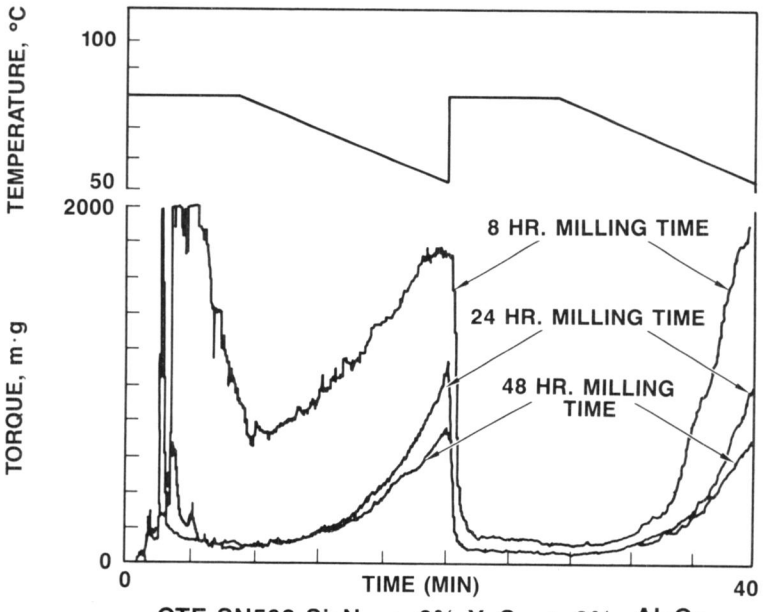
40 KSI — 7 HR, 22 MIN	40 KSI — 0	
40 KSI — 17 HR, 19 MIN	30 KSI — 1 MIN	
30 KSI — 100 HR (SURVIVED)	30 KSI — 3 HR, 38 MIN	
	30 KSI — 4 HR, 55 MIN	

SPA 8794-1

TASK VII EXPERIMENTAL MATRIXES

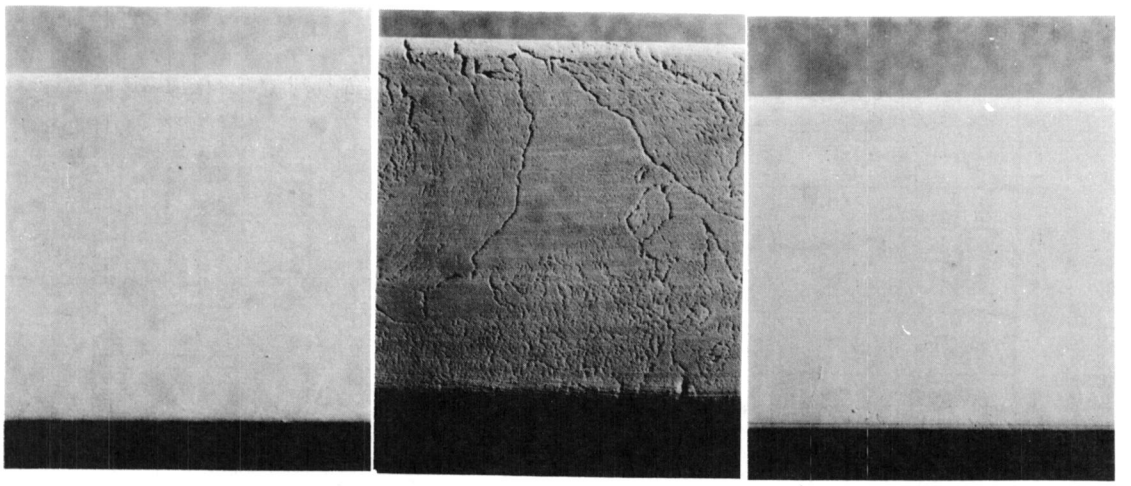
PROCESS VARIABLE	EXPERIMENTAL MATRIX NUMBER						
	1	2	3	4	5	6	7
RAW MATERIAL	X				X	X	
BINDER		X			X	X	X
BINDER EXTRACTION			X			X	X
INJECTION MOLDING			X			X	
POWDER PREPARATION (MILLING)			X		X		
COMPOSITION				X			
SINTERING	X			X		X	

MIXING BEHAVIOR COMPARISON ON TORQUE RHEOMETER



GTE SN502 Si_3N_4 + 6% Y_2O_3 + 2% Al_2O_3
AT 15.5% BINDER

AS INJECTED TEST BAR SURFACES



A. 8 HR. MILLING
99°C (210°F) MOLDING

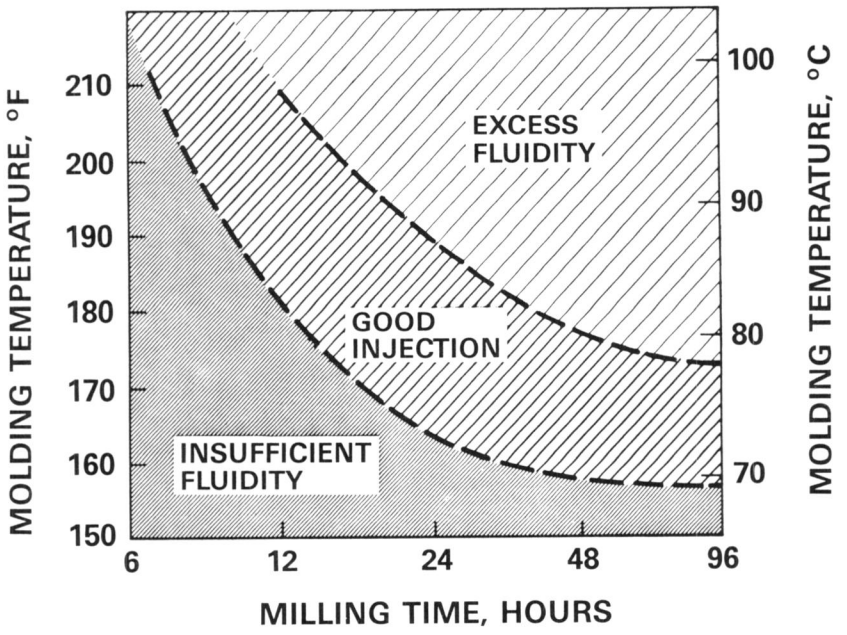
B. 8 HR. MILLING
77°C (170°F) MOLDING

C. 24 HR. MILLING
77°C (170°F) MOLDING

GTE SN502 Si_3N_4 + 6% Y_2O_3 + 2% Al_2O_3 AT 15.5% BINDER

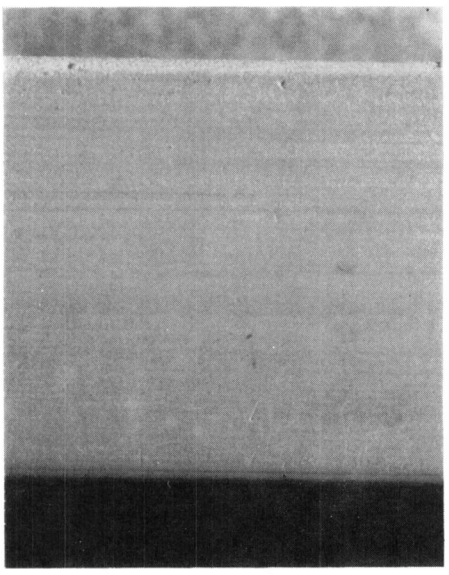
SPA 8687-119

FLOW CHARACTERISTICS OF INJECTION MOLDING



NASA IMPROVED Si_3N_4

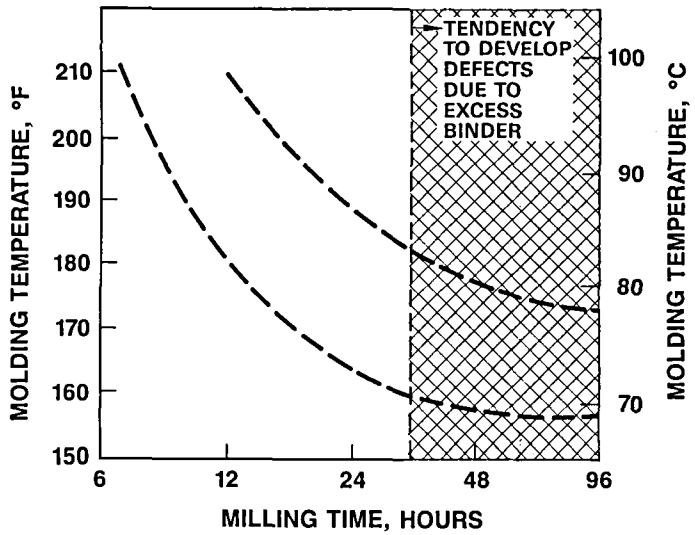
SURFACE CHANGE DURING DEWAX — 96 HOUR MILLED POWDER



AS INJECTED

DEWAXED

DEWAX EFFECT



GTE SN502 +6% Y_2O_3 + 2% AL_2O_3 AT 15% BINDER

NASA IMPROVED Si_3N_4

TASK II EXPERIMENTAL MATRIX
1/2 REPLICATE OF A 2^5 FRACTIONAL FACTORIAL DESIGN

		C+				C−			
		D+		D−		D+		D−	
		E+	E−	E+	E−	E+	E−	E+	E−
A+	B+		abcd	abce		abde			ab
	B−	acde			ac		ad	ae	
A−	B+	bcde			bd		bd	be	
	B−		cd	ce		de			1

A = CONSOLIDATION METHODS — SINTER/HIP CYCLE (A−) VS CYCLE (A+)

B = CONSOLIDATION ENVIRONMENT — WITHOUT POWDER BED (B−) VS WITH POWDER BED (B+)

C = MIXING — SIGMA MIXER (C−) VS SIGMA MIXER PLUS EXTRUDER (C+)

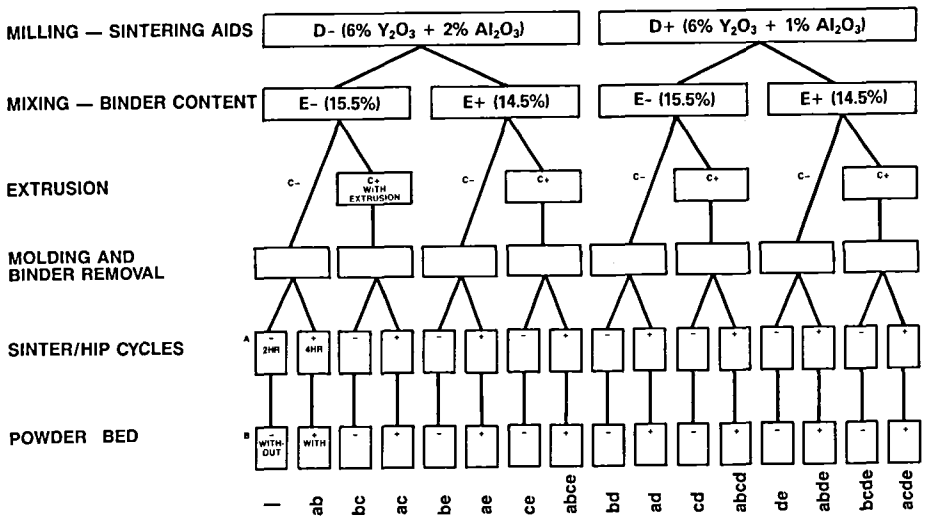
D = SINTERING AIDS — (6% Y_2O_3 + 2% Al_2O_3) (D−) VS (6% Y_2O_3 + 1% Al_2O_3) (D+)

E = BINDER CONTENT — 15.5% (E−) VS 14.5% (E+)

SPA 8962-97A

NASA IMPROVED Si_3N_4

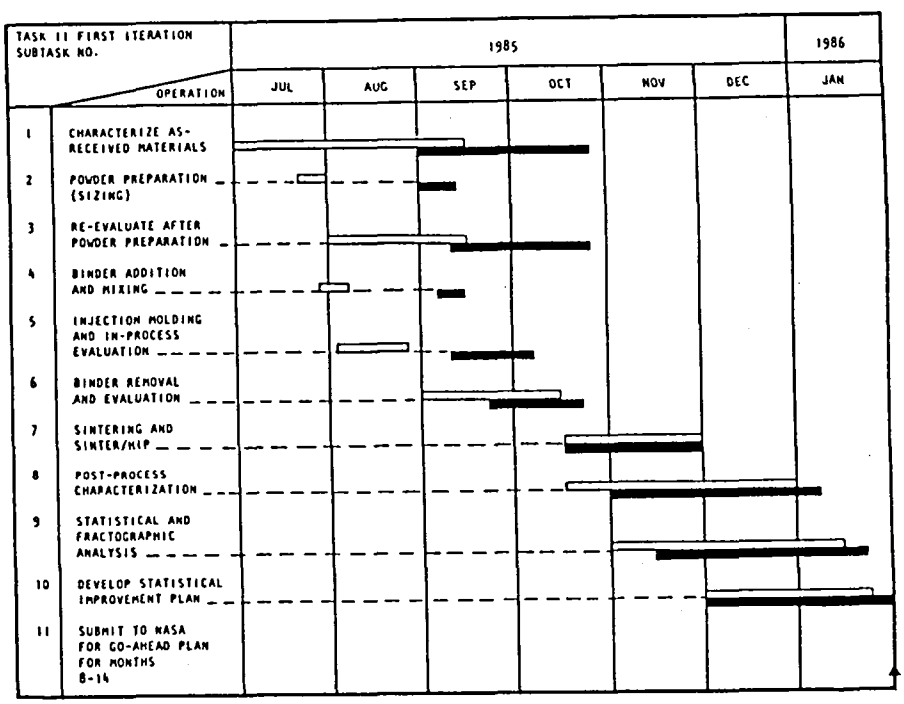
EXPERIMENTAL MATRIX PROCESS FLOW CHART



SPA 8687-98A

TASK II — MOR BAR MATRIX STUDY

MONTHS 1 THROUGH 7



TASK II TORQUE CHARACTERIZATION

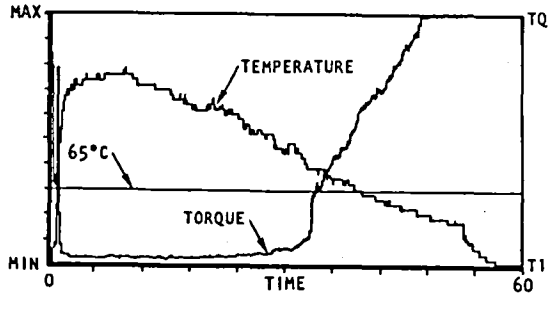
MIXING VARIATION	TORQUE AT 65°C (150°F), m·g			
	D– (6% Y_2O_3 + 2% Al_2O_3)		D+ (6% Y_2O_3 + 1% Al_2O_3)	
	E– (15.5% BINDER)	E+ (14.5% BINDER)	E– (15.5% BINDER)	E+ (14.5% BINDER)
MATRIX II-1 INJECTION MOLDING BATCHES				
C–	1450	1500	1386	1544
C+ (EXTRUDED)	1100	1452	762	1290
MATRIX II-2 INJECTION MOLDING BATCHES				
C–	876	1304	948	1175
C+ (EXTRUDED)	439	796	500	748

NOTES

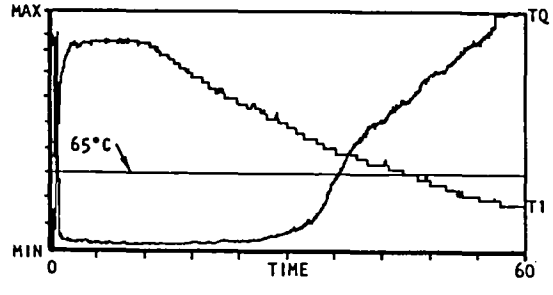
1. VALUES ARE FROM SINGLE MIXER RUNS
2. MIXER COOLING RATE WAS 1°C (1.8°F) PER MINUTE
3. m·g = meter·gram

MATRIX II-1 TORQUE CHARACTERIZATION

EFFECT OF BINDER CONTENT ON RHEOLOGY



15.5% BINDER



14.5% BINDER

MATRIX II-1 AND II-2 X-RADIOGRAPHIC YIELD

AS-INJECTED BARS

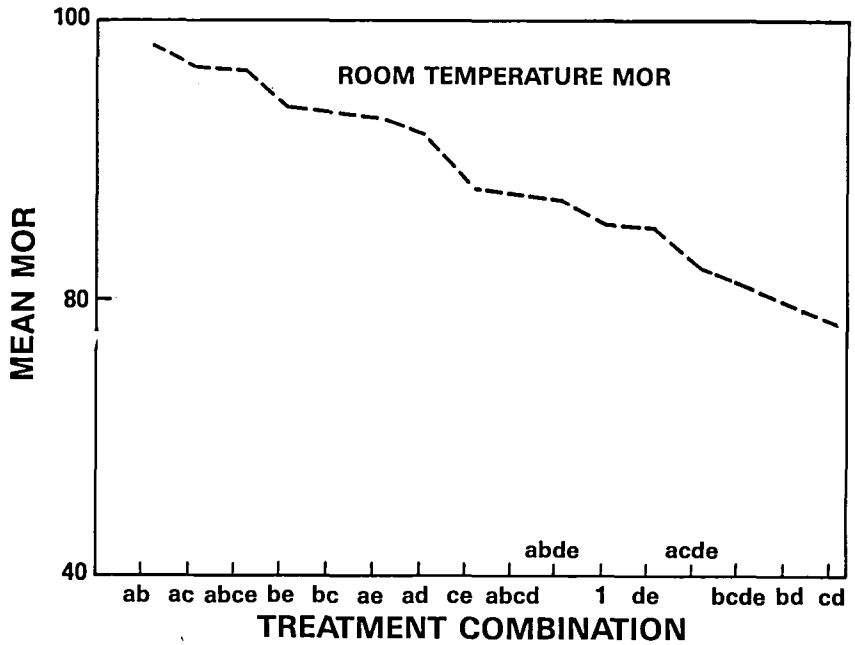
MIXING PROCEDURE	YIELD IN PERCENT			
	D− (6% Y_2O_3 + 2% Al_2O_3)		D+ (6% Y_2O_3 + 1% Al_2O_3)	
	E− (15.5% BINDER)	E+ (14.5% BINDER)	E− (15.5% BINDER)	E+ (14.5% BINDER)
	MATRIX II-1, STARCK H-1 Si_3N_4, 200 BARS INJECTED FOR EACH CONDITION			
C−	77	77	69	76
C+ (EXTRUDED)	87	92	68	92
	MATRIX II-2, DENKA 9FW Si_3N_4, 160 BARS INJECTED FOR EACH CONDITION			
C−	95	95	95	95
C+ (EXTRUDED)	96	96	98	96

ROOM TEMPERATURE MOR AND WEIBULL SLOPE (MATRIX II-2)

PROCESSING CONDITION	AVERAGE STRENGTH,* ksi	WEIBULL SLOPE
1	82.90	6.97
ab	97.25	13.63
bc	91.96	7. 66
ac	95.58	12.73
be	92.18	10.15
ae	91.56	10.13
bd	76.20	12.84
de	82.84	7.01
ce	85.69	7.94
abce	95.28	13.44
abcd	85.02	11.24
abde	84.84	19.93
bcde	77.73	9.74
acde	78.95	5.32
ad	89.30	12.18
cd	74.40	5.64

*30 SAMPLES TESTED FOR EACH CONDITION

MATRIX II-2 MOR (DENKA 9FW)



STATISTICAL ANALYSIS

MATRIX II-2

- PROCESSING FACTORS HAVING SIGNIFICANT EFFECTS ON MOR

  A, B AND D

- TWO FACTOR INTERACTIONS HAVING SIGNIFICANT EFFECTS ON MOR

  B × C, B × D AND C × D

NOTE: A — SINTERED/HIP
B — POWER BED
C — MIXING
D — SINTERING AID

SINTER/HIP CYCLE EFFECT

MATRIX II-2

SINTERING/HIP 2 HRS	SINTERING/HIP 4 HRS
83.2 ksi	89.8 ksi

DIFFERENCE = 6.6 ksi

POWDER BED AND SINTERING AIDS EFFECTS

MATRIX II-2

	(B+) PB*	(B−) NO PB*
(D+) 6% Y_2O_3 + 2% Al_2O_3	81.0 Ksi	81.6 Ksi
(D−) 6% Y_2O_3 + 1% Al_2O_3	94.3 Ksi	89.1 Ksi

*PB: POWDER BED

POWDER BED AND MIXING METHOD EFFECTS

MATRIX II-2

	(B+) PB*	(B−) NO PB*
(C+) SIGMA MIXER AND EXTRUDER	87.7 Ksi	83.9 Ksi
(C−) SIGMA MIXER	87.6 Ksi	86.8 Ksi

*PB: POWDER BED

SUMMARY

- AVERAGE STRENGTH AND WEIBULL MODULUS OF BASELINE AS-PROCESSED, RANDOMLY SELECTED INJECTION MOLDED, SINTERED Si_3N_4 SAMPLES ARE 547 MPa (79.3 ksi) AND 7.9 RESPECTIVELY
- STRENGTH AND AS-PROCESSED SURFACE QUALITY ARE CLOSELY RELATED
- TORQUE RHEOMETRY HAS THE POTENTIAL TO PREDICT INJECTION MOLDING BEHAVIOR
- GOOD QUALITY AS-INJECTED BARS CAN DEGRADE DURING DEWAX IF THEY ARE PROCESSED WITH EXCESS BINDER
- FINAL TEST BAR PROPERTIES STRONGLY DEPEND ON EACH PROCESSING STEP

(CONTINUED)

SUMMARY

- A MATERIAL WITH A MEAN STRENGTH OF 97 Ksi AND A WEIBULL MODULUS OF 14 HAS BEEN DEVELOPED BY A STATISTICALLY DESIGNED MATRIX EXPERIMENT
- STATISTICAL ANALYSIS CAN IDENTIFY KEY PROCESSING PARAMETERS AND PROCESSING VARIATIONS

IMPROVED PROCESSING OF Si_3N_4

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Cleveland, Ohio 44135

and

George Y. Baaklini
Cleveland State University
Cleveland, Ohio 44115

A sintered Si_3N_4-SiO_2-Y_2O_3 composition, NASA 6Y, was developed that reached four-point flexural average strength/standard deviation values of 857/36, 544/33, and 462/59 MPa at room temperature, 1200 and 1370 °C respectively. These strengths represented improvements of 56, 38, and 21 percent over baseline properties at the three test temperatures. At room temperature the standard deviation was reduced by more than a factor of three. These accomplishments were realized by the iterative utilization of conventional x-radiography to characterize structural (density) uniformity as affected by systematic changes in powder processing and sintering parameters. Accompanying the improvement in mechanical properties was a change in the type of flaw causing failure from a pore to a large columnar ß-Si_3N_4 grain typically 40-80 μm long, 10-30 μm wide, and with an aspect ratio of 5:1.

IMPROVED PROCESSING OF Si_3N_4

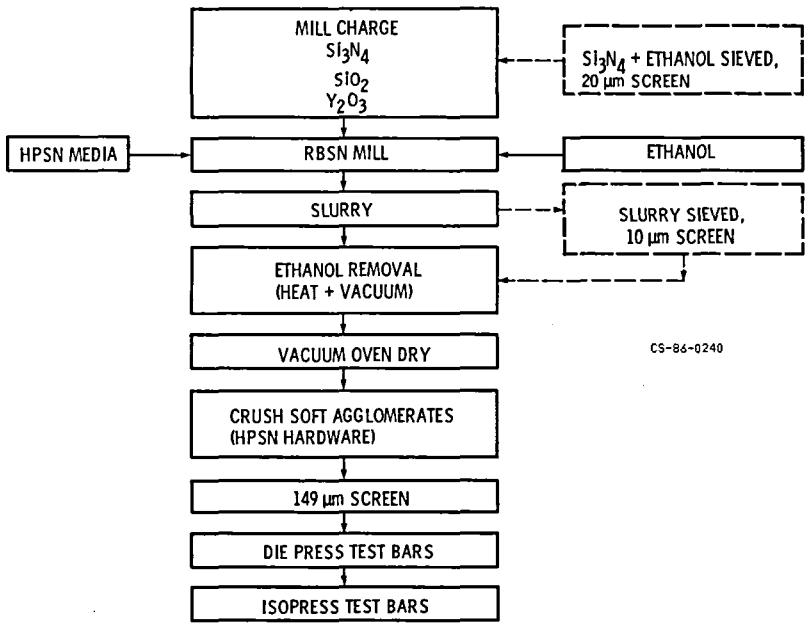
OBJECTIVE

TO IMPROVE THE STRENGTH AND UNIFORMITY OF SINTERED SILICON NITRIDE BY A SYSTEMATIC INVESTIGATION OF POWDER PROCESSING AND SINTERING VARIABLES AS THEY AFFECT RADIO GRAPHICALLY CHARACTERIZED DENSITY GRADIENTS, AND CONSEQUENTLY THE STRENGTH LEVEL AND SCATTER OF SILICON NITRIDE

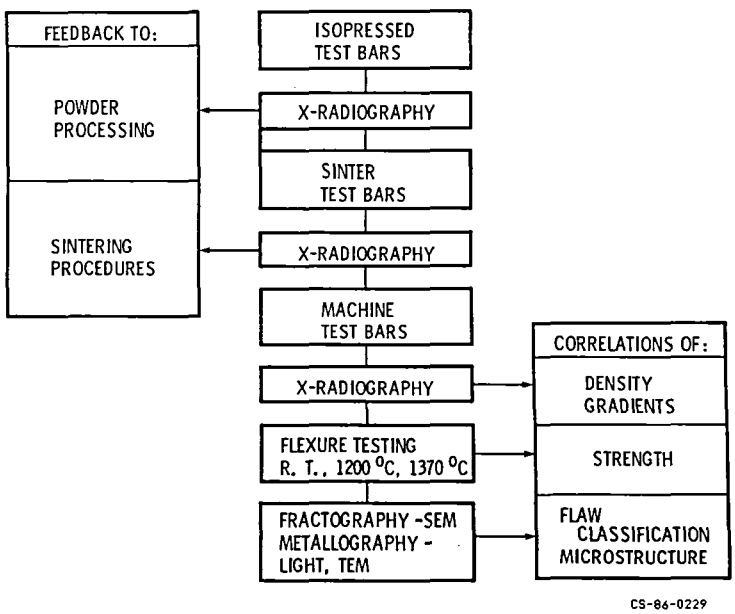
CHARACTERIZATION OF SILICON NITRIDE AND OXIDE POWDERS

MATERIAL	SOURCE	MANUFACTURERS DESIGNATION	PURITY, %	SPECIFIC SURFACE AREA, $m^2 \cdot g^{-1}$	X-RAY DIFFRACTION ANALYSIS, %			CHEMICAL ANALYSIS		
					α	β	FREE Si	OXYGEN, wt %	CARBON, wt %	SPECTROGRAPHIC ANALYSIS, ppm
Si_3N_4	KBI-AME	HIGH PURITY	99.5	4.7	83.7	15.7	0.6	0.89	0.18	240Al, 60Ca, 20Co, 50Cr, 1280Fe, 20Mg, 30Mn, 40Ti, 40V, 590Y, 30Zn, 10Zr
SiO_2	APACHE CHEMICALS	6846	99.99	166	----	----	---	----	.16	220Al, 150Ca, 30Cr, 50Cu, 50Fe, 130Mg, 90Mn, 340Na, 40Ti
Y_2O_3	MOLYCORP	5600	99.9	7.5	----	----	---	---	.11	60Cu, 60Mg, 40 R.E. OXIDES

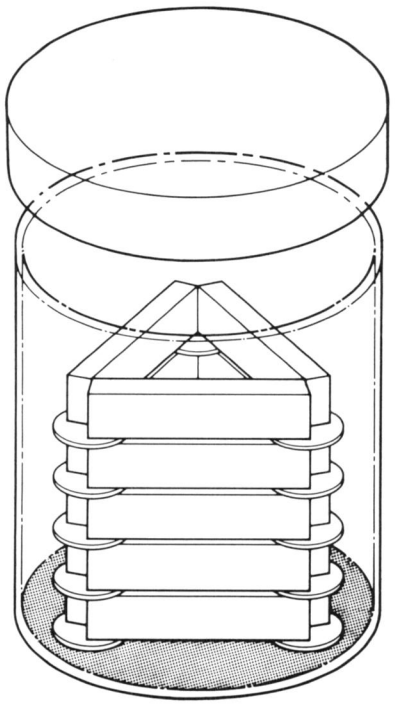
POWDER PROCESSING OF NASA 6Y Si_3N_4



EVALUATION OF NASA 6Y Si_3N_4

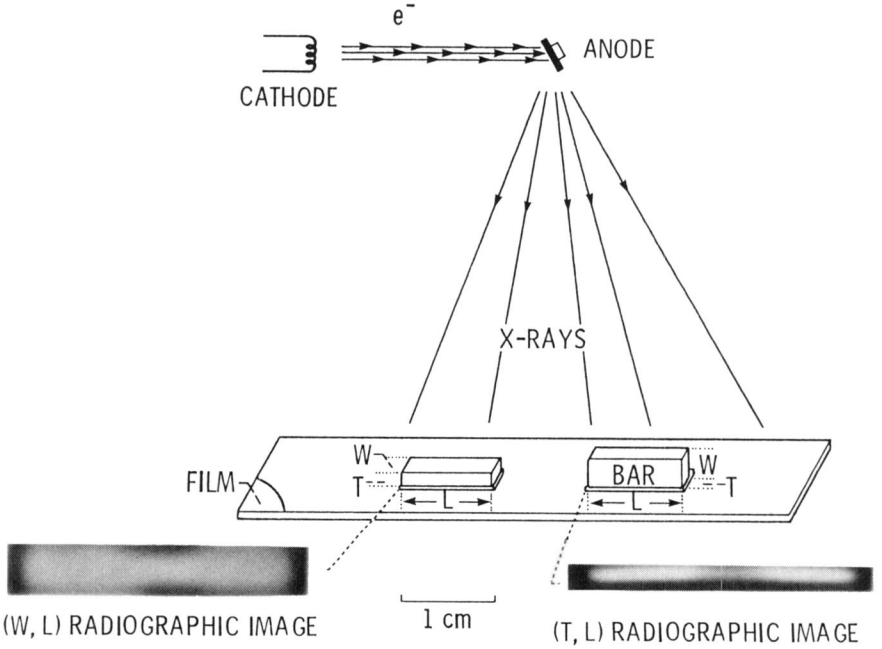


Si_3N_4 BAR/BN SETTER ARRANGEMENT IN W SINTER CUP



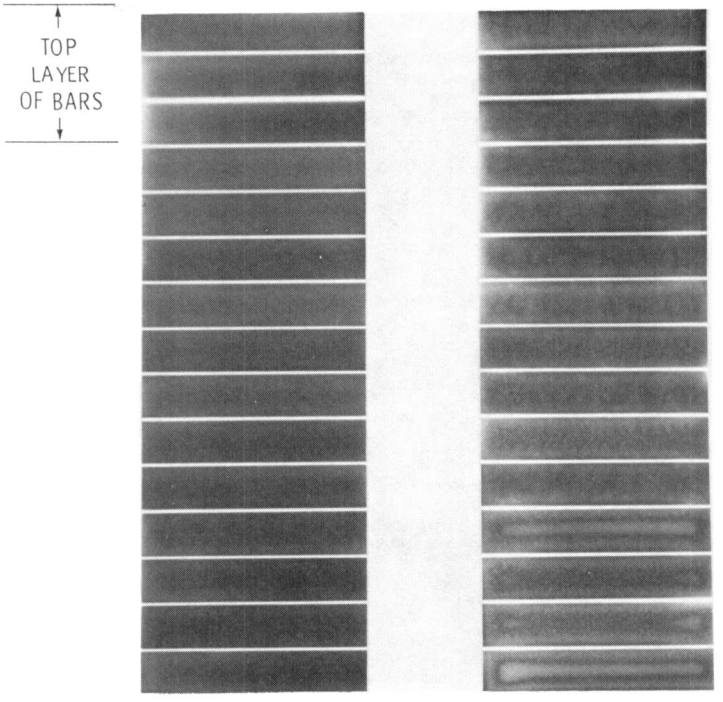
CS-86-0235

CONVENTIONAL RADIOGRAPHY OF NASA 6Y Si_3N_4 TEST BARS



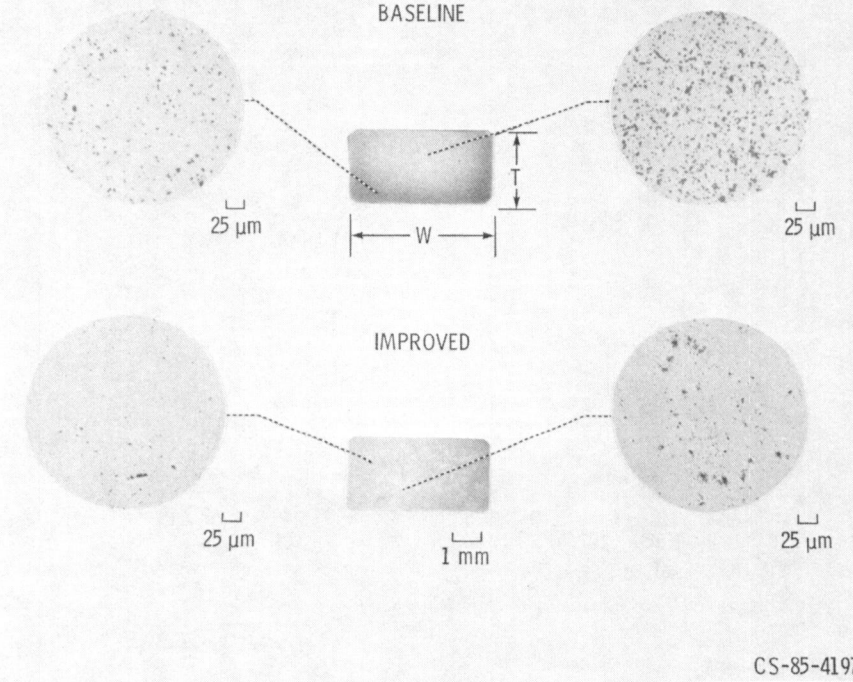
CS-85-4207

RADIOGRAPHS OF 15-BAR SINTER-GROUPS OF NASA 6Y Si_3N_4



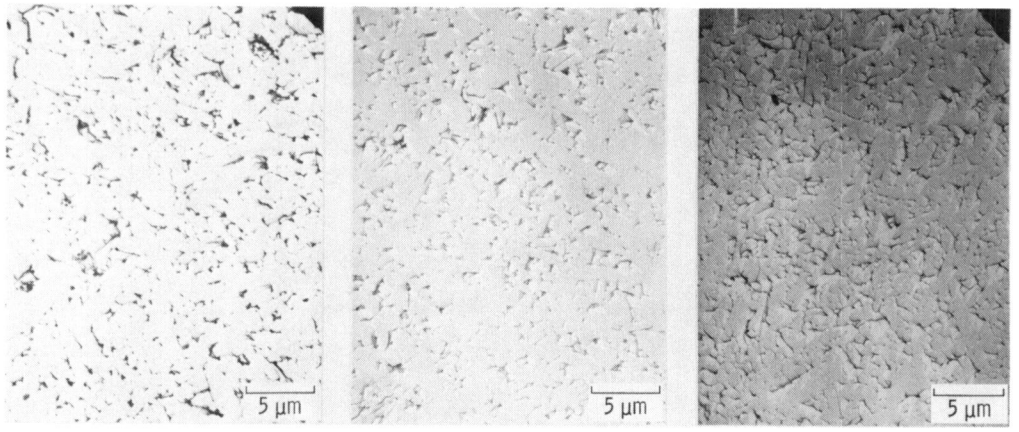
CS-85-4205

CASE-CORE STRUCTURE COMPARISON FOR BASELINE AND IMPROVED NASA 6Y Si_3N_4



CS-85-4197

TEM MICROSTRUCTURES OF NASA 6Y Si_3N_4 EFFECT OF GRINDING TIME



tg = 24 hr	tg = 100 hr	tg = 300 hr
0.3 - 4.0 μm EQUIAX 0.35 - 3.5 μm COLUM. WIDTH 1:2 TO 1:6 ASPECT RATIO 70 VOL. % COLUM.	0.2 - 3.5 μm EQUIAX 0.4 - 2.0 μm COLUM. WIDTH 1:2 TO 1:14 ASPECT RATIO 40 VOL. % COLUM.	0.2 - 3.0 μm EQUIAX 0.25 - 2.0 μm COLUM. WIDTH 1:2 TO 1:8 ASPECT RATIO 20 VOL. % COLUM.

CS-85-4209

SINTERING CONDITIONS AND RESULTS FOR Si_3N_4-SiO_2-Y_2O_3
COMPOSITION NASA 6Y SINTERED AT 2140 °C

NASA 6Y BATCH NUMBER	MILLING TIME, hr	SINTERING CONDITIONS			SINTERING RESULTS[a]		
		TIME, hr	PN, MPa	BN SETTER CONTACT	AVERAGE WEIGHT LOSS, %	AVERAGE WIDTH SHRINKAGE, %	AVERAGE MACHINED DENSITY, $g\text{-}cm^{-3}$
BASELINE	24	1	2.5	MAX	3.85	15.6	3.12
11	100	↓	↓	MAX	5.14	17.6	3.23
13	100	↓	↓	MIN	4.93	17.6	3.24
12	300	↓	↓	MAX	5.74	18.0	3.25
14	300	↓	↓	MIN	5.42	17.5	3.24
15	24	2	5.0	↓	5.10	17.2	3.22
16	24	↓	↓	↓	4.44	16.8	3.23
17	100	↓	↓	↓	4.39	17.3	3.23
20	100	↓	↓	↓	2.81	17.2	3.22
25	300	↓	↓	↓	4.88	17.8	3.28
28[b]	100	↓	↓	↓	3.77	17.3	3.21
29[b, c]	100	↓	↓	↓	3.06	16.1	3.23
31[b, c]	300	↓	↓	↓	3.71	17.3	3.24
21 (2050 °C)	100	↓	↓	↓	1.65	14.9	3.05

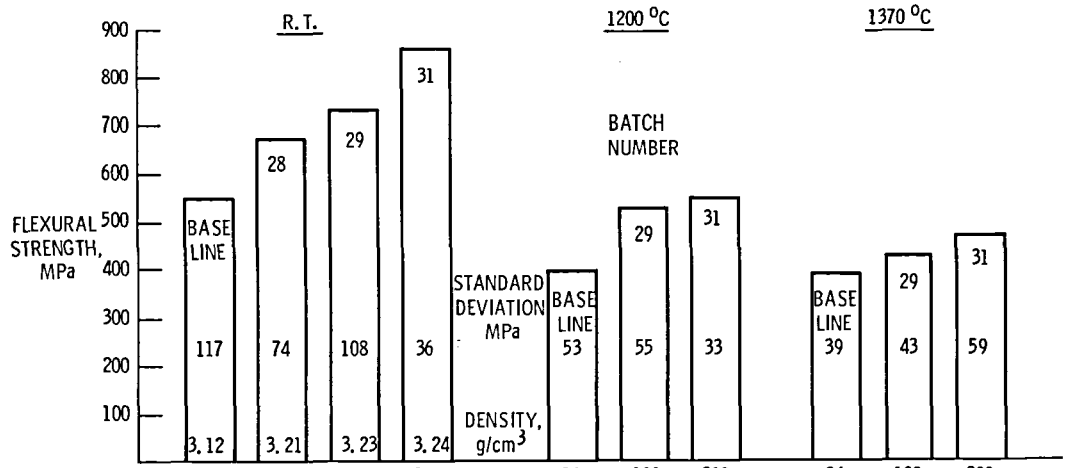
[a]AVERAGE FOR EACH COMPOSITION REPRESENT 30 BARS EXCEPT FOR BASELINE WHICH REPRESENTS 150 BARS AND BATCH 28 WHICH REPRESENTS 15 BARS.

[b]SINTER CUP RAISED 3.8 cm.

CS-86-0223

[c]Si_3N_4 POWDER WET SIEVED BEFORE AND AFTER MILLING.

COMBINED EFFECT OF MODIFIED PROCESSING/SINTERING PROCEDURES ON THE FLEXURAL STRENGTH OF NASA 6Y Si_3N_4



t_g, h	24	100	100	300	24	100	300	24	100	300
t_s, h	1	2	2	2	1	2	2	1	2	2
P_N, MPa	2.5	5.0	5.0	5.0	2.5	5.0	5.0	2.5	5.0	5.0
B_N	max.	min.	min.	min.	max.	min.	min.	max.	min.	min.
SINTER HT. ADJ.		√	√	√		√	√		√	√
POWDER WET SIEVE			√	√		√	√		√	√

CS-86-0232

ASSESSMENT OF FRACTURE ORIGINS FOR NASA 6Y SINTERED Si_3N_4

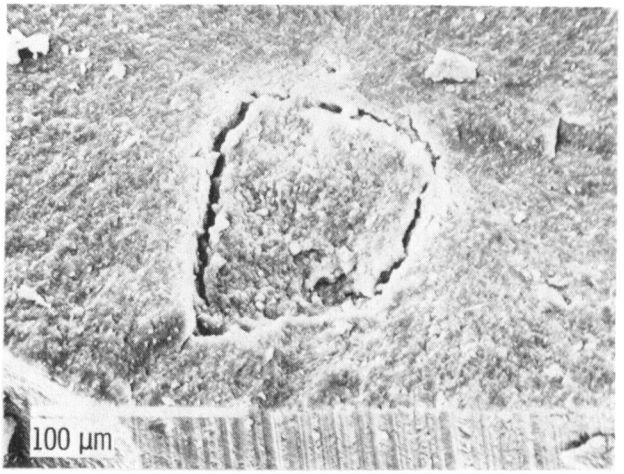
			SUB-SURFACE PORE	SURFACE PORE	SEAM	SUB-SURFACE AGGLOMERATE	COLUMNAR GRAIN	SURFACE DEFECT	METALLIC INCLUSION
R.T. FLEXURE TEST	TOTAL FRACTURE ORIGINS IDENTIFIED	192[a]	56	44	28	25	17	13	9
	PERCENT OF TOTAL	100	29	23	14	13	9	7	5
1200 °C FLEXURE TEST	TOTAL FRACTURE ORIGINS IDENTIFIED	90[a]	23	19	9	7	14	0	18
	PERCENT OF TOTAL	100	26	21	10	8	15	0	20
1370 °C FLEXURE TEST	TOTAL FRACTURE ORIGINS IDENTIFIED	127[a]	30	15	25	3	32	0	22
	PERCENT OF TOTAL	100	24	12	20	2	25	0	17

[a]NUMBER EXCLUDES 111, 47, AND 41 BARS FOR R.T., 1200 °C, AND 1370 °C, RESPECTIVELY, WHERE FLAW REGION OR FLAW TYPE COULD NOT BE DETERMINED.

CS-86-0234

CRITICAL FLAWS IN R. T. FRACTURE OF NASA 6Y Si_3N_4

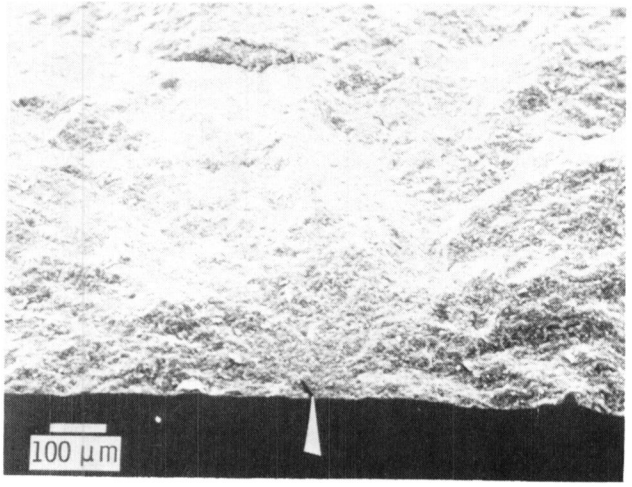
SURFACE PORE, σ_F = 620 MPa

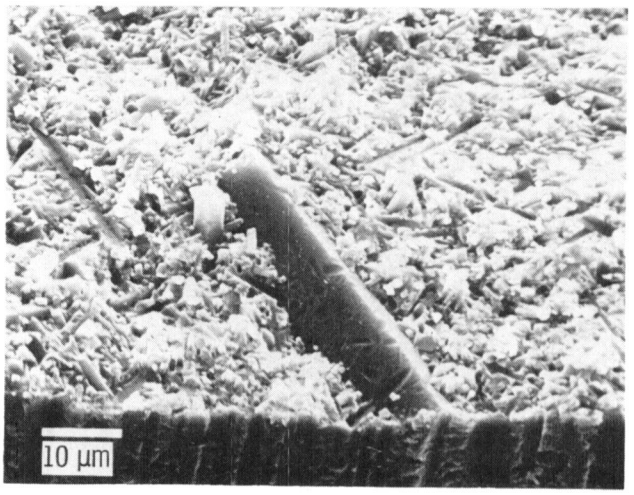


AGGLOMERATE, σ_F = 470 MPa

CS-85-4199

COLUMNAR Si_3N_4 GRAIN CRITICAL FLAW IN R. T. FRACTURE OF IMPROVED NASA 6Y Si_3N_4



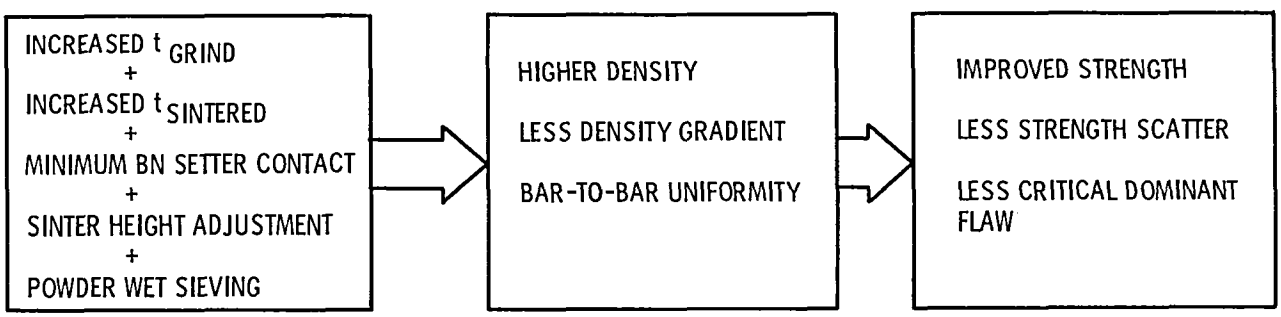


σ_F = 905 MPa

CS-85-4201

SUMMARY

APPLICATION OF CONVENTIONAL RADIOGRAPHY VERY BENEFICIAL IN GUIDING POWDER PROCESSING AND SINTERING PARAMETER CHANGES FOR IMPROVED Si_3N_4



COLLOIDAL CHARACTERIZATION OF SILICON NITRIDE AND SILICON CARBIDE*

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Case Western Reserve University
Cleveland, Ohio 44106

The colloidal behavior of aqueous ceramic slips strongly affects the forming and sintering behavior and the ultimate mechanical strength of the final ceramic product. The colloidal behavior of these materials, which is dominated by electrical interactions between the particles, is complex due to the strong interaction of the solids with the processing fluids. A surface titration methodology, modified to account for this interaction, has been developed and used to provide fundamental insights into the interfacial chemistry of these systems. Various powder pretreatment strategies were explored to differentiate between true surface chemistry and artifacts due to exposure history. The colloidal behavior of both silicon nitride and carbide is dominated by silanol groups on the powder surfaces. However, the colloid chemistry of silicon nitride is apparently influenced by an additional amine group. With the proper powder treatments, silicon nitride and carbide powder can be made to appear colloidally equivalent. The impact of these results on processing control will be discussed.

*Work done under NASA Grant NAG3-468.

WHY?

* SINTERING OF COVALENT SOLIDS REQUIRES SUBMICRON PARTICLES (PROCESSING COLLOIDAL DISPERSIONS)

  -- CERAMIC POWDERS ACQUIRE SURFACE CHARGE AND INTERACT WITH IONS IN PROCESSING FLUID

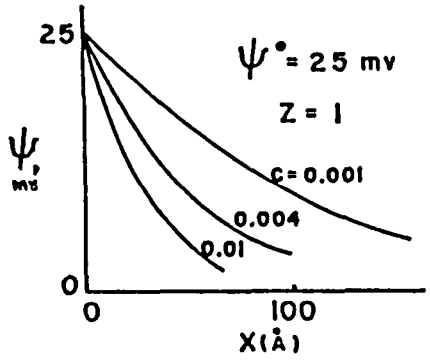
  -- STABILITY AND RHEOLOGY DOMINATED BY ELECTROSTATIC EFFECTS

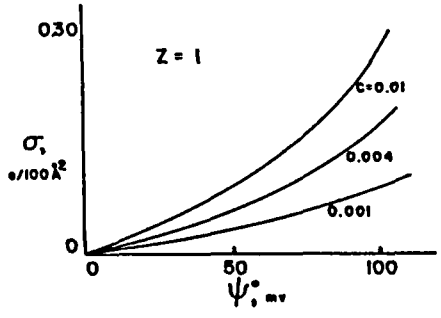
* STRONG CORRELATION BETWEEN DISPERSION QUALITY AND FINAL PROPERTIES OF SINTERED CERAMIC

TECHNIQUES

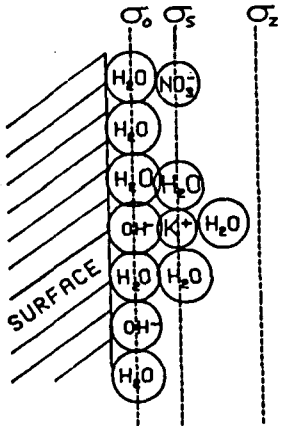
- SPECTROSCOPIC CHARACTERIZATION
  FTIR, ESCA, SIMS, AUGER
- ELECTROPHORETIC CHARACTERIZATION
  ZETA POTENTIAL
- TITRATION OF SURFACE GROUPS
  SURFACE CHARGE
- RHEOLOGICAL CHARACTERISTICS
  VISCOMETRY
- STABILITY CHARACTERIZATION
  SEDIMENTATION

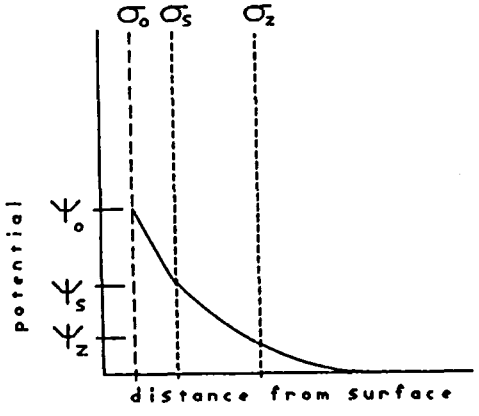
RELATIONSHIP BETWEEN SURFACE POTENTIAL AND SURFACE CHARGE

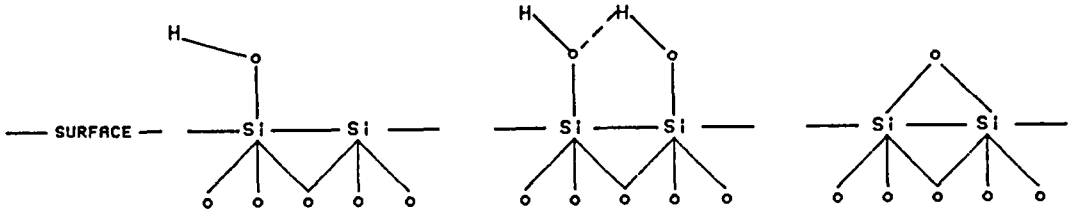




DEVELOPMENT OF SURFACE CHARGE AND SURFACE POTENTIAL







FREE SURFACE SILANOL

HYDROGEN - BONDED SURFACE SILANOL

HYDROPHOBIC SILOXANE

ADSORPTION OF POTENTIAL DETERMINING IONS:

$$\equiv Si\text{-}OH + OH^- \rightleftharpoons \equiv Si\text{-}O^- + H_2O$$

$$\equiv Si\text{-}OH + H^+ \rightleftharpoons \equiv Si\text{-}OH_2^+$$

ORIGIN OF SURFACE POTENTIAL

REVERSIBLE ELECTRODE --

NERNST EQUATION RELATES SURFACE POTENTIAL (Ψ_o) TO CONCENTRATION OF POTENTIAL DETERMINING IONS:

$$\Psi_o = \frac{2.303RT}{ZF} \text{LOG}(C/C_{ZP})$$

AMPHOTERIC OXIDE --

ASSUMING H^+ AND OH^- ARE POTENTIAL DETERMINING AND EXHIBIT NERNSITAN BEHAVIOR:

$$\Psi_o = 59.7(pH_{PZC} - pH)$$

ORIGIN OF SURFACE SPECIES -- THERMODYNAMICS OF THE DOUBLE LAYER

SITE MODEL OF SOLID/LIQUID INTERFACE:

$$MH_2^+ \rightleftharpoons MH + H^+$$

$$MH \rightleftharpoons M^- + H^+$$

EQUATE CHEMICAL POTENTIALS:

BULK COMPONENTS--

$$\mu_j = \mu_j^\circ + RT \ln a_j$$

SURFACE SITES--

$$\mu_{hj} = \mu_{hj}^\circ + RT \ln a_{hj} + ZF\zeta$$

EXPERIMENTAL APPROACH

-- IDENTIFY PRETREATMENT METHOD TO YIELD REPRODUCIBLE, PRISTINE SURFACE

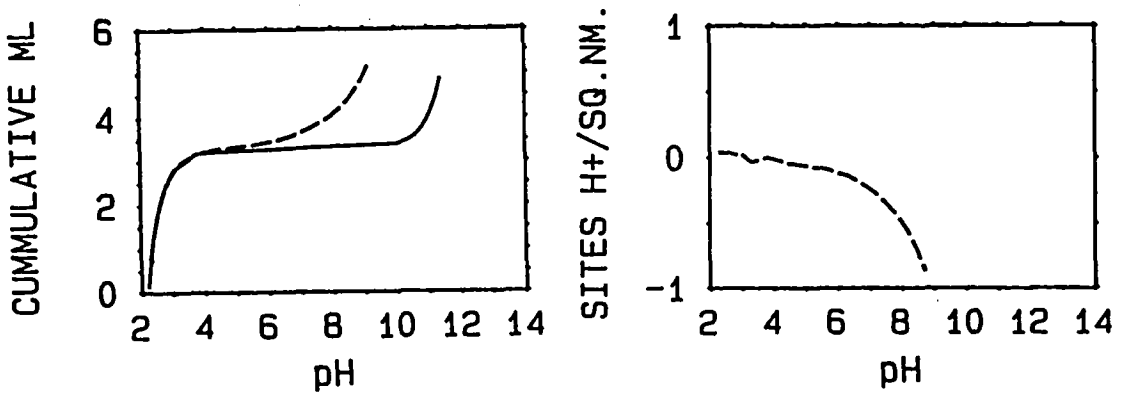
-- INVESTIGATE EFFECT OF MANUFACTURING HISTORY, SUBSTRATE ON ADSORPTION

-- COMPARE SILICON NITRIDE, SILICON CARBIDE AND SILICA

-- EXPLORE THE ROLE OF ELECTROLYTE

-- COMPARE TITRATION RESULTS WITH RESULTS FROM OTHER METHODS

POTENTIOMETRIC TITRATION



FOR AMPHOTERIC COLLOID:

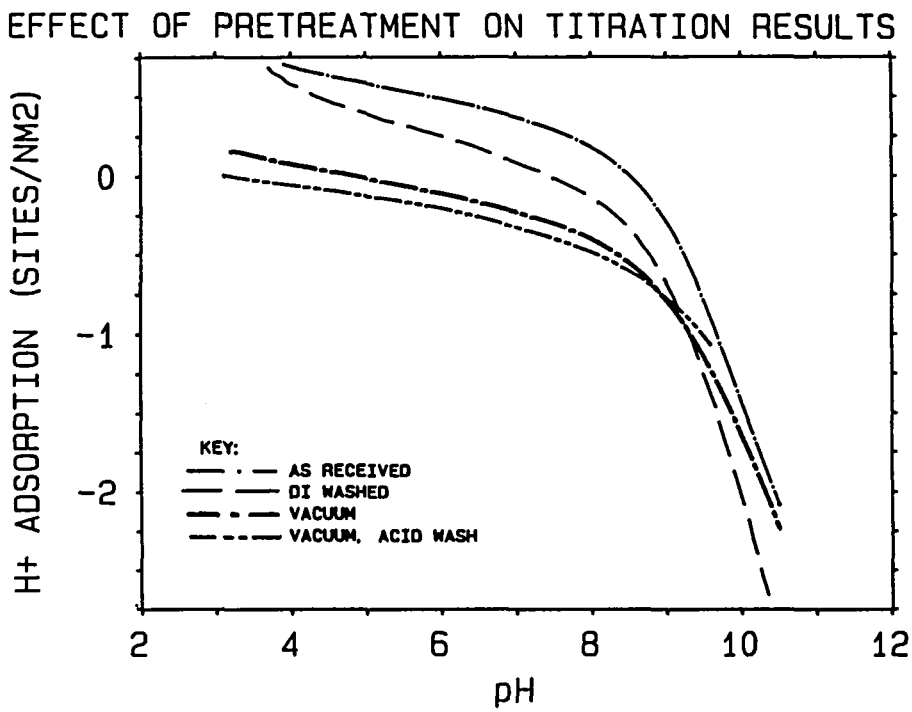
$$\sigma_o = F (\Gamma_{H+} - \Gamma_{OH-})$$

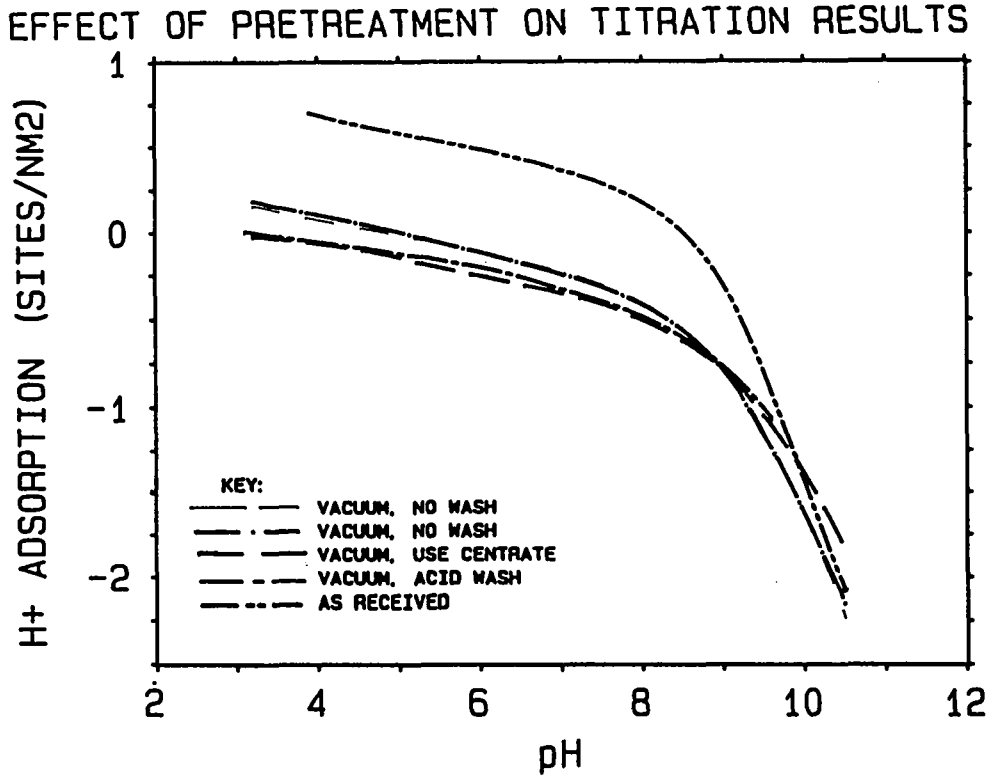
WHERE F = FARADAY'S CONSTANT

Γ_{H+} . Γ_{OH-} = EQUIVALENTS OF H+ OR OH- BOUND TO SURFACE

HANDLING AND PRETREATMENT:

* NONE (AS RECEIVED)
* FIRE 500°C IN ARGON
* FIRE 300°C IN OXYGEN
* WASH IN DI WATER, THEN:
  -- NO DRY
  -- DRY, MILD CONDITIONS
  -- DRY RAPIDLY
* WASH IN ACIDIC ELECTROLYTE
* EXPOSE TO MODERATE VACUUM





SUMMARY OF RESULTS

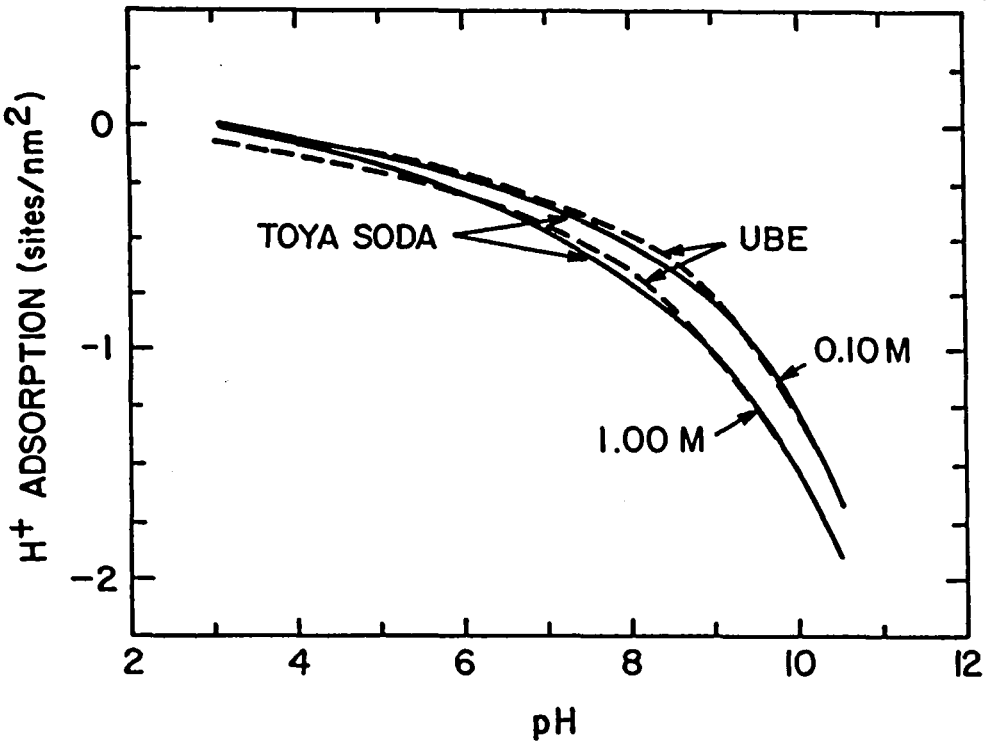
* PHYSISORBED SPECIES REMOVED
  - BAKE IN DRY ENVIRONMENT
  - EXPOSE TO MODERATE VACUUM

* CHEMISORBED SPECIES DESORB RAPIDLY IN ACIDIC ELECTROLYTE

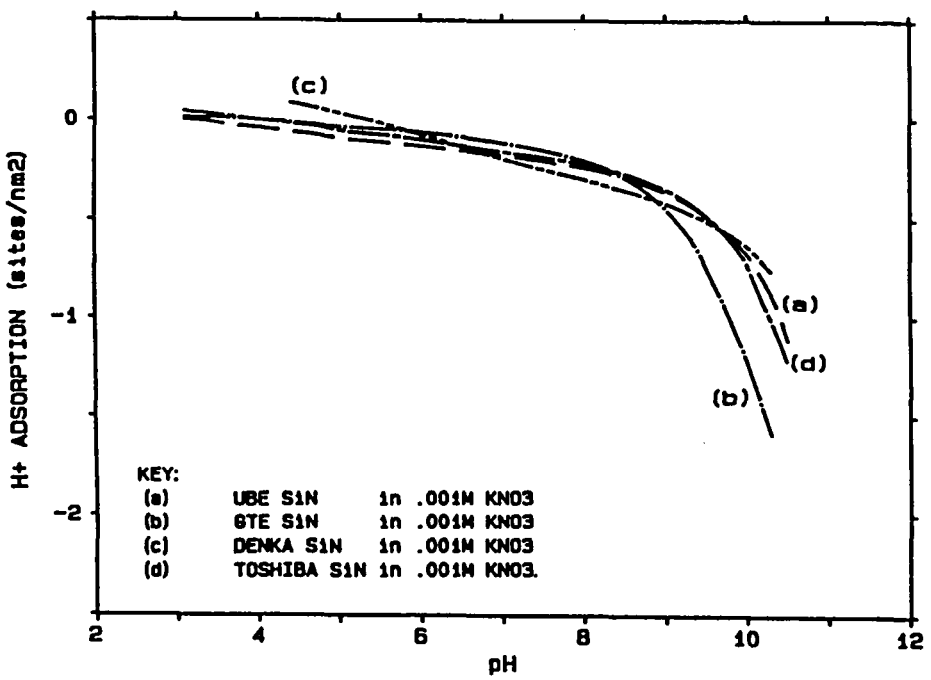
* SILICON NITRIDE REACTS WITH AQUEOUS SOLUTION TO RE-FORM ORIGINAL ADSORBED SPECIES

* WASHING IN ACIDIFIED SOLUTION REMOVES ALL ADSORBATE, BUT LEAVES SURFACE UNALTERED FROM "AS RECEIVED" STATE

COMPARISON OF UBE AND TOYA SODA SILICON NITRIDE



COMPARISON OF SILICON NITRIDE FROM FOUR MANUFACTURERS



HYPOTHESES

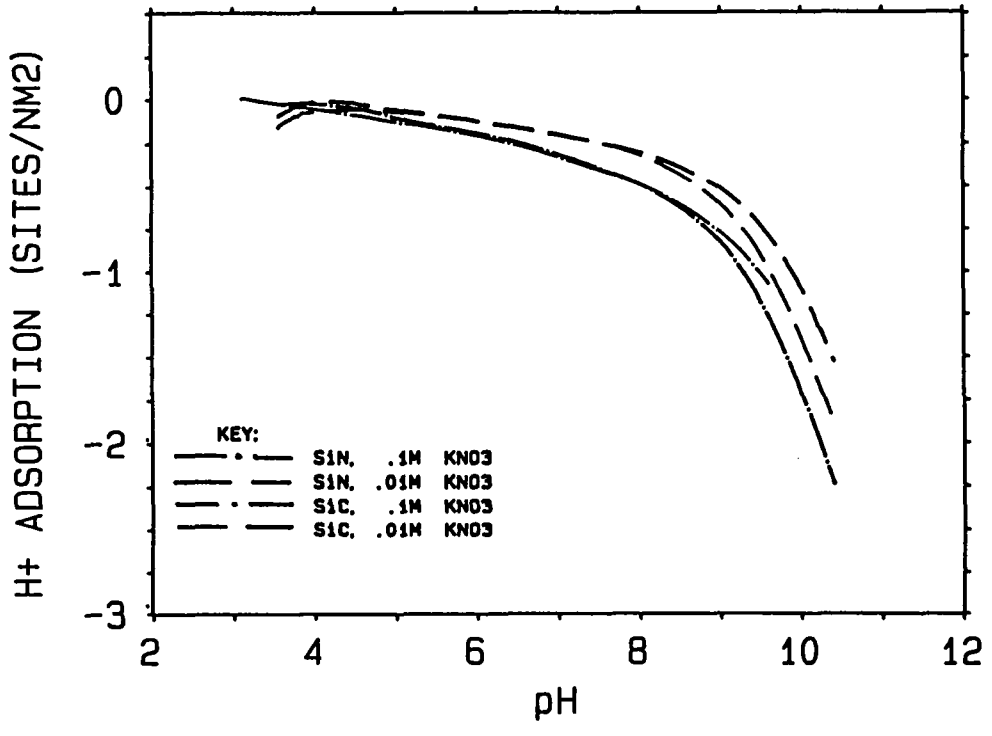
* TITRATABLE SURFACE SPECIES IS SILICA

* SPECIES ADSORBED ON SILICON NITRIDE IS AMMONI
  - MOST PHYSISORBED, SOME CHEMISORBED
  - SIMILAR TO REPORTED ADSORPTION OF AMMONIA ON SILICA

* AMMONIA IS FORMED BY HYDROLYSIS OF SILICON NITRIDE:

$$6\ H_2O + Si_3N_4 \longrightarrow 3\ SiO_2 + 4\ NH_3$$

COMPARISON OF SILICON NITRIDE AND SILICON CARBIDE



SUMMARY OF SURFACE TITRATION DATA

* SUGGEST PZC < pH 3 FOR BOTH SILICA AND SILICON CARBIDE

* SUGGEST PZC > pH 6 FOR MOST SILICON NITRIDES

* LITTLE DIFFERENCE AMONG VARIOUS MANUFACTURERS OF SILICON NITRIDE

* LITTLE DIFFERENCE BETWEEN SILICON NITRIDE AND SILICON CARBIDE Si-OH SITE DENSITY

* WITH CAREFUL PRETREATMENT, DATA IS REPRESENTATIVE OF NATIVE SURFACE AND IS REPRODUCIBLE

NDE OF STRUCTURAL CERAMICS BY PHOTOACOUSTIC MICROSCOPY

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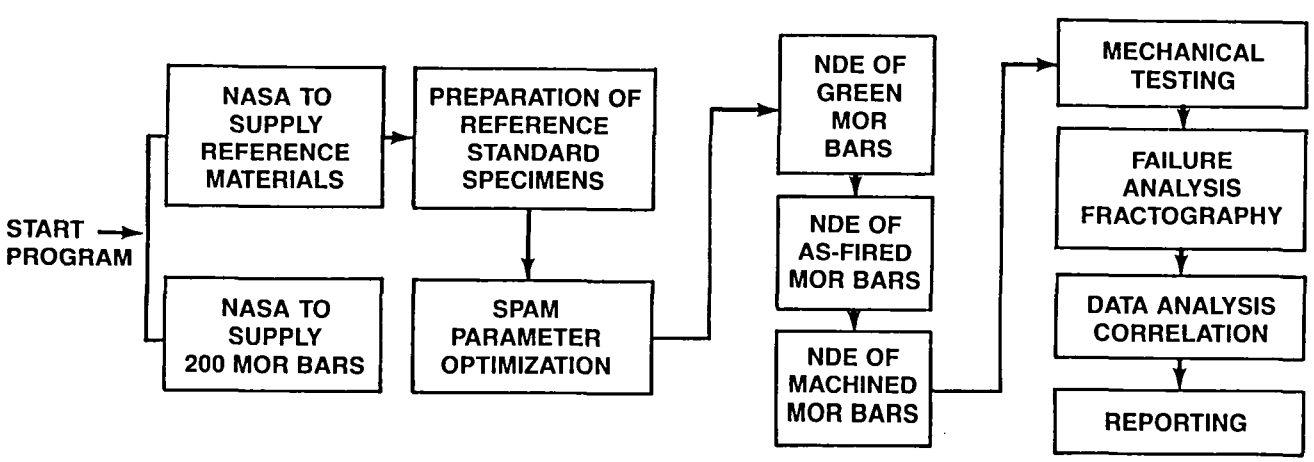
Photoacoustic microscopy (PAM) has been utilized to detect surface and subsurface defects in structural ceramic materials. A computerized PAM data acquisition, color imaging and analysis system has been developed and used under this program. Subsurface simulated cylindrical holes can be detected to about 1 mm below the interrogating surface. Simulated tight surface cracks of 96 μm length and 48 μm depth can be detected in these materials under optimum conditions.

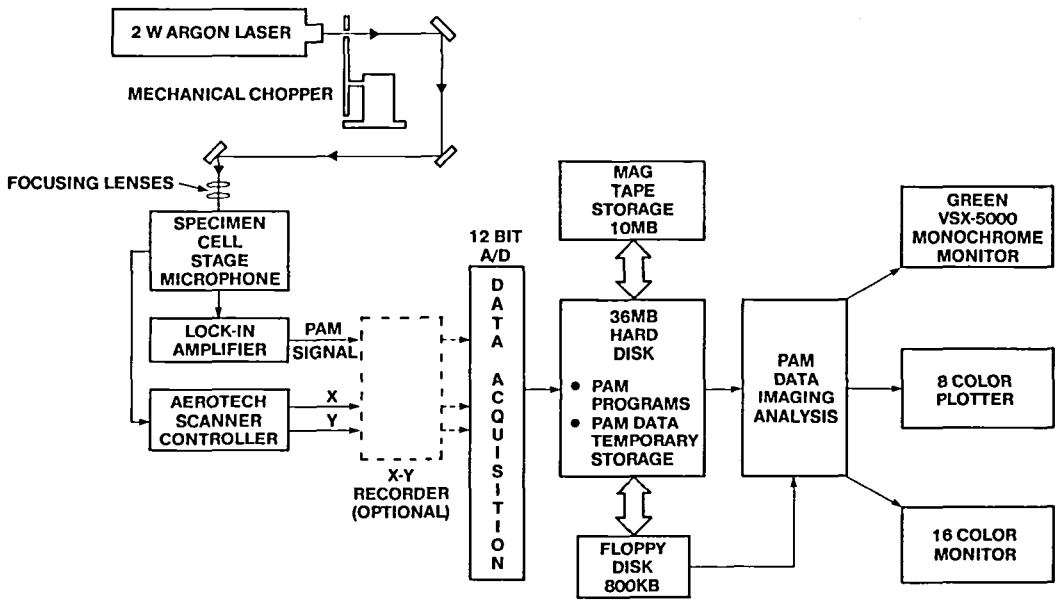
OBJECTIVES

- o DEVELOP COMPUTERIZED CAPABILITY TO DIGITALLY ACQUIRE/RETRIEVE AND IMAGE PAM SIGNALS
- o DEVELOP CAPABILITY TO DETECT 250μM SIZE VOIDS/INCLUSIONS 1MM BELOW INTERROGATING SURFACE
- o DEVELOP CAPABILITY TO DETECT SURFACE CONNECTED CRACKS
- o DEMONSTRATE ABILITY OF NDE TO PREDICT FAILURE SITE ON MOR BAR CONTAINING NATURAL FLAWS

NDE OF STRUCTURAL CERAMICS BY PHOTOACOUSTIC MICROSCOPY



PAM FLAW DETECTION
DATA ACQUISITION AND IMAGING SYSTEM



PAM DATA ACQUISITION AND IMAGING-ANALYSIS SYSTEM

DATE 4/10/86

CHART NO. PKK

FEATURES

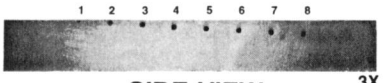
- o SCANNER
  - o PROGRAMMABLE X-Y RASTER SCAN
  - o 2μM AXIS RESOLUTION
- o DATA ACQUISITION/IMAGING
  - o MENU DRIVEN ALGORITHMS
  - o ACQUIRES AND STORES DATA
  - o 12 BIT A/D RESOLUTION
  - o MONOCROME AND COLOR DISPLAY
  - o 8 COLOR PLOTTER
  - o EXPERIMENTAL STATISTICS
  - o MAGNIFICATION/ZOOM
  - o PAN
  - o THRESHOLDING
  - o FLAW/PAM SIGNAL SIZING
  - o HISTOROGRAM OF PAM SIGNALS

GT-8040(7-84)

PAM FLAW DETECTION
BATCH-A AS-FIRED Si_3N_4

TOP VIEW 3X

HOLE #



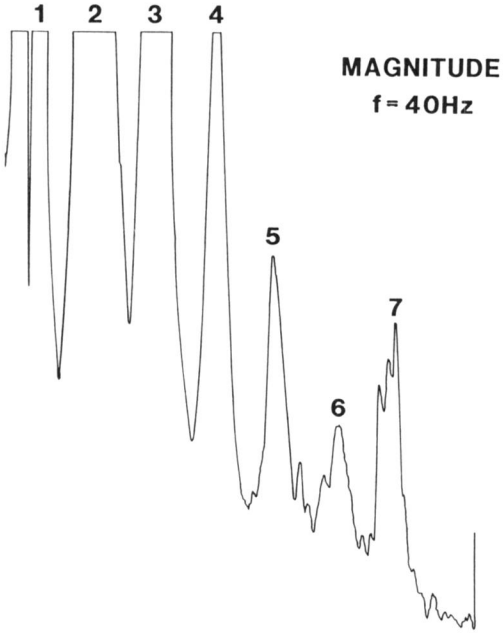
SIDE VIEW 3X

HOLE #	HOLE LOCATION FROM TOP SURFACE μm
1	OPEN TO SURFACE
2	VERY NEAR TO SURFACE BUT NOT OPEN
3	156
4	390
5	547
6	665
7	825
8	1015

NOMINAL DIAMETER ≈ 375μm
NOMINAL DISTANCE BETWEEN HOLES ≈ 2.5 mm
APPROXIMATE DEPTH ≈ 3.125 mm

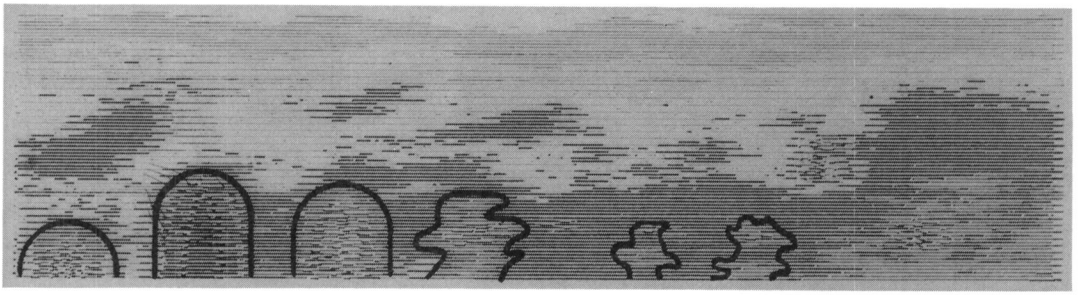
VS85-1814

PAM SUBSURFACE FLAW DETECTION
AS-FIRED SILICON NITRIDE

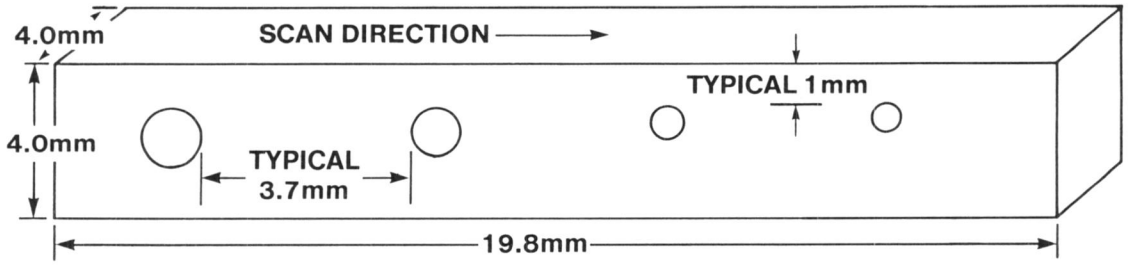


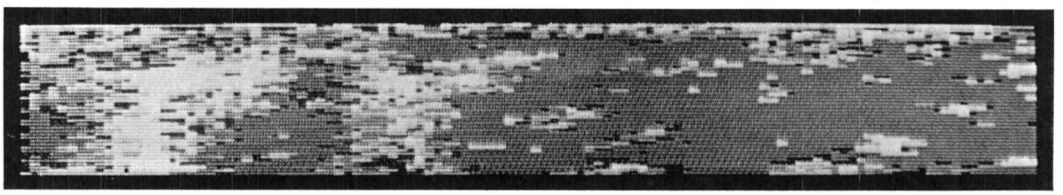
VS86-1813

PAM DIGITAL IMAGING-
SUBSURFACE FLAWS
BATCH-A AS-FIRED Si_3N_4



PAM SUBSURFACE FLAW DETECTION
AS FIRED SINTERED SILICON CARBIDE





HOLE DIA. μm 1000 750 500 250

PHOTOACOUSTIC MICROSCOPY
SURFACE CRACK DETECTION

DATE 4/10/86
CHART NO. PKK

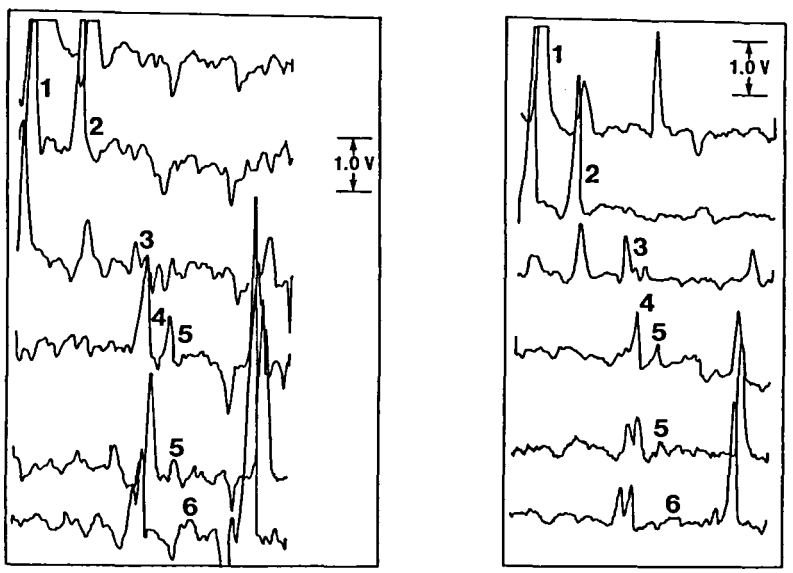
Crack #	Load (Kg)	Crack		Signal-to-Noise Ratio	
		Length (2c) μm	Depth* (a) μm	40 Hz 250μm/sec. 200 μV	300 Hz 250μm/sec 50 μV
1	12	401	200	Saturated	Saturated
2	10	323	162	9.0	13.5
3	5	234	117	2.0	4.5
4	4	205	102	3.0	5.5
5	2	140	70	N.D.	2.0
6	1	96	48	N.D.	N.D.

*Assuming semicircular flaw, a = c

N.D. - Signal-to-noise ratio of 1
Difficult to separate the flaw signal from the background

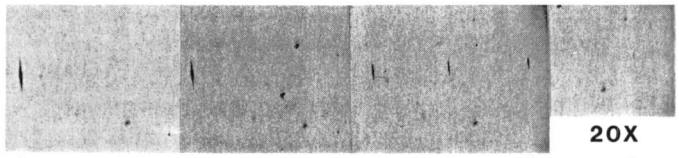
GT-8040(7-84)

PHOTOACOUSTIC MICROSCOPY SURFACE CRACK DETECTION

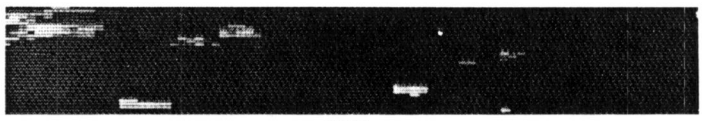


VS86-1810

PHOTOACOUSTIC MICROSCOPY
SURFACE CRACK DETECTION



OPTICAL



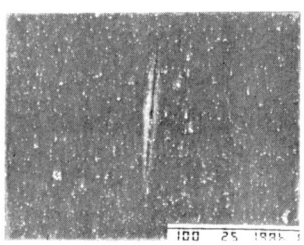
40Hz

300Hz

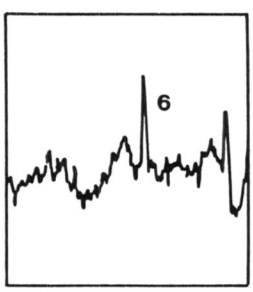
DIGITAL IMAGE

VS86-1811

PHOTOACOUSTIC MICROSCOPY
SURFACE CRACK DETECTION

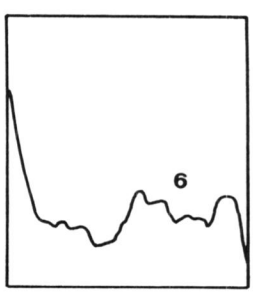


$2C = 96\mu m$
$a = 48\mu m$



50μm/SEC

$HPSi_3N4$
f=40Hz



250μm/SEC

VS86-1812

MOLTEN SALT CORROSION OF SIC AND SI_3N_4

N. S. Jacobson, J. L. Smialek, and D. S. Fox
NASA Lewis Research Center
Cleveland, Ohio

The most severe type of corrosion encountered in heat engines is corrosion by molten sodium sulfate, which is formed by the reaction of ingested sodium chloride and sulfur impurities in the fuel. This problem has been studied extensively for superalloys, but only recently examined for ceramics. Our program at Lewis addresses this problem with laboratory studies to understand the fundamental reaction mechanisms and with burner studies to provide a more realistic simulation of the conditions encountered in a heat engine. In addition we are assessing the effect of corrosion on the strengths of these materials. Each of these aspects will be reviewed and some ideas toward possible solutions will be discussed.

THE HOT CORROSION PROBLEM

- FORMATION OF Na_2SO_4

$$2NaCl + SO_2 + \frac{1}{2}O_2 + H_2O = Na_2SO_4 + 2HCl$$

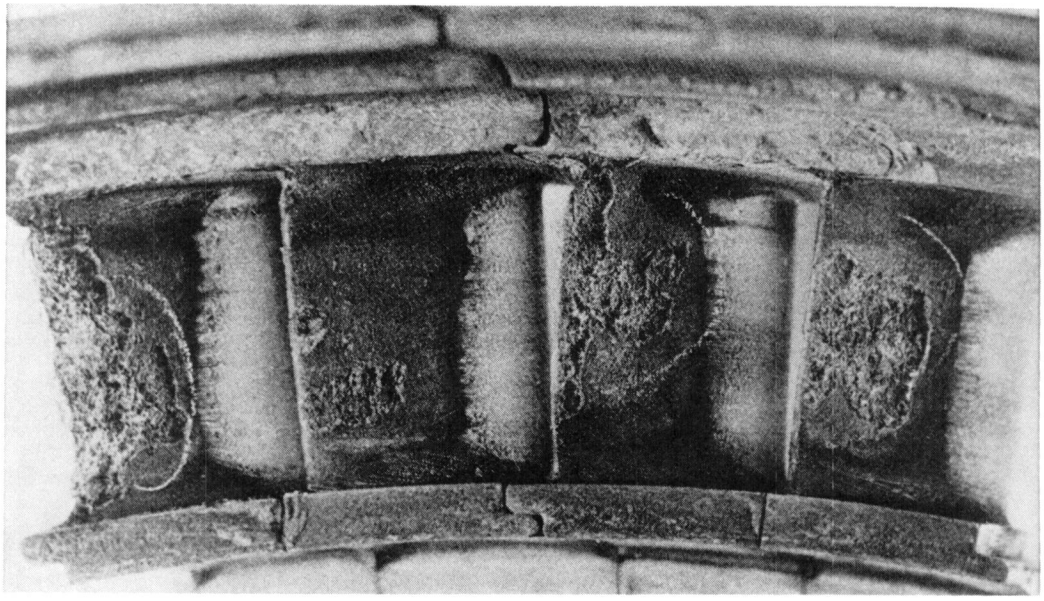
- DEPOSITION OF MOLTEN Na_2SO_4 ON ENGINE PARTS

  FUNCTION OF T, P, [SALT]

- POTENTIALLY CATASTROPHIC ATTACK

CS-86-1388

TURBINE VANE HOT CORROSION



CS-73740

BASIC AND ACIDIC MOLTEN SALTS

- $Na_2SO_4 = Na_2O + SO_3 = 2Na^+ + O^= + SO_3$ $\quad K = 4.6 \times 10^{-16}$ AT 1000 °C

  LOW P_{SO_3} - HIGH a_O = - BASIC

  HIGH P_{SO_3} - LOW a_O = - ACIDIC

- $Na_2CO_3 = Na_2O + CO_2 = 2Na^+ + O^= + CO_2$ $\quad K = 9.7 \times 10^{-7}$ AT 1000 °C

  MODEL BASIC SALT

CS-86-1383

REACTIONS WITH MOLTEN SALTS

- DISSOLUTION OF PROTECTIVE OXIDE (MO) BY MOLTEN SALT
- UNPROTECTED METAL OR CERAMIC SUSCEPTIBLE TO ATTACK
- TYPES OF DISSOLUTION
  - ACIDIC $\quad MO = M^{++} + O^=$
  - BASIC $\quad MO + O^= = MO_2^=$
- SiO_2 IS AN ACIDIC OXIDE
  - EXPECT REACTION WITH BASIC SALT
  - $SiO_2 + O^= = SiO_3^=$
  - SILICATES LIQUID T 780 °C

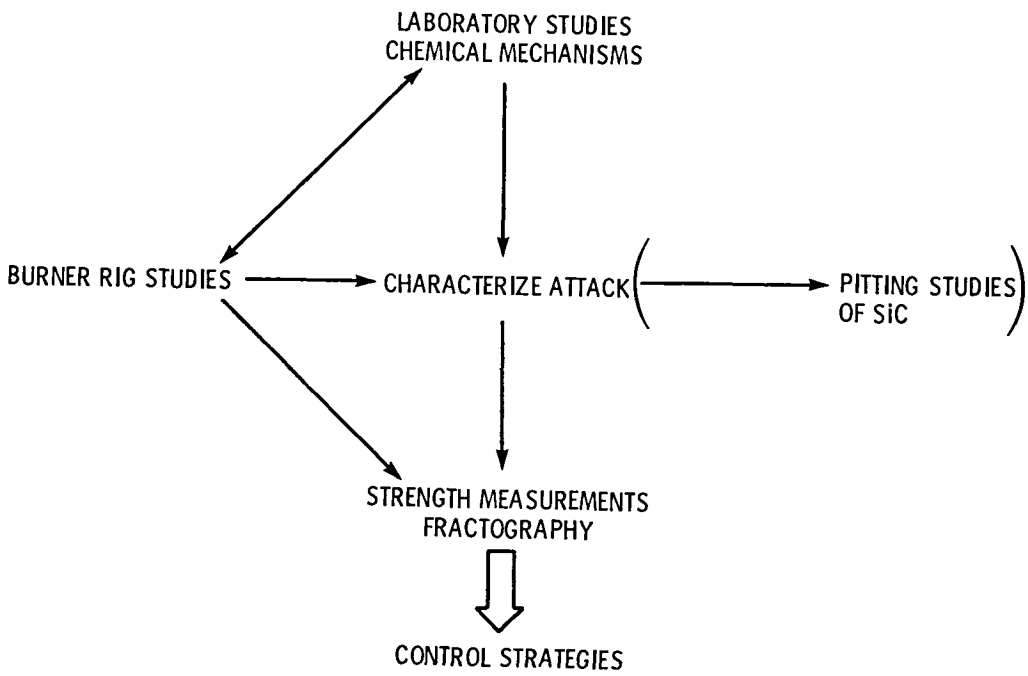
CS-86-1384

EXPERIMENTAL TECHNIQUES

- LABORATORY
  - AIRBRUSH SAMPLE WITH SALT; HEAT
  - PRECISELY CONTROL PARAMETERS
  - MONITOR KINETICS, MICROSTRUCTURAL CHANGES
  - ONE TIME DEPOSITION OF SALT
- BURNER
  - JET FUEL SEEDED WITH NaCl
  - CONTINUOUS DEPOSITION OF SALT; CLOSER TO ENGINE CONDITIONS
  - DIFFICULT TO CONTROL PARAMETERS

CS-86-1382

LEWIS CORROSION STUDIES OF SiC AND Si_3N_4



CS-86-1379

MATERIALS STUDIED

- SINTERED α-SiC (B, C)

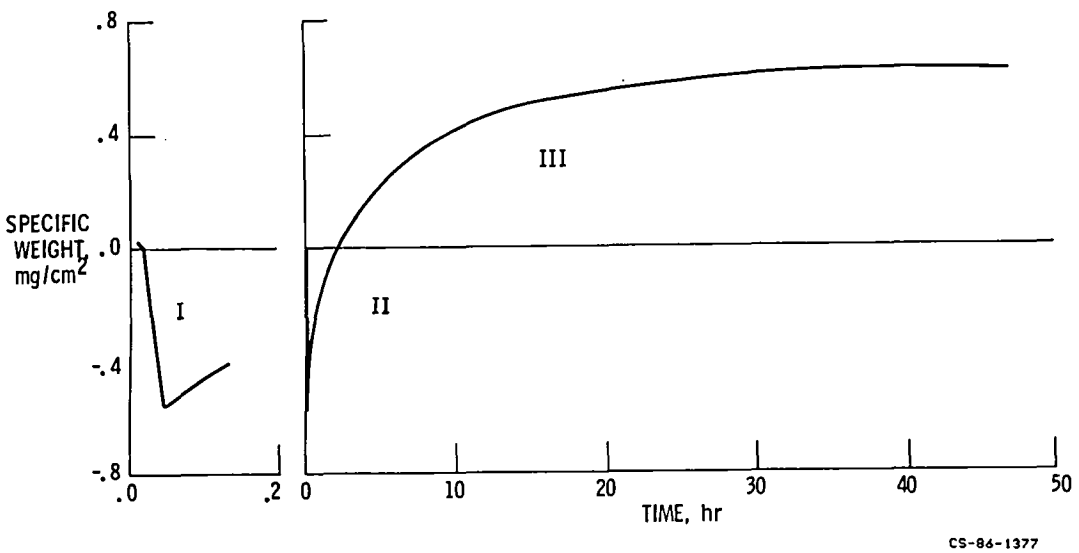
  HP SiC, CVD SiC, SC SiC

- SINTERED Si_3N_4 (Al_2O_3, Y_2O_3)

  SINTERED Si_3N_4 (Y_2O_3), HIP'd RB Si_3N_4

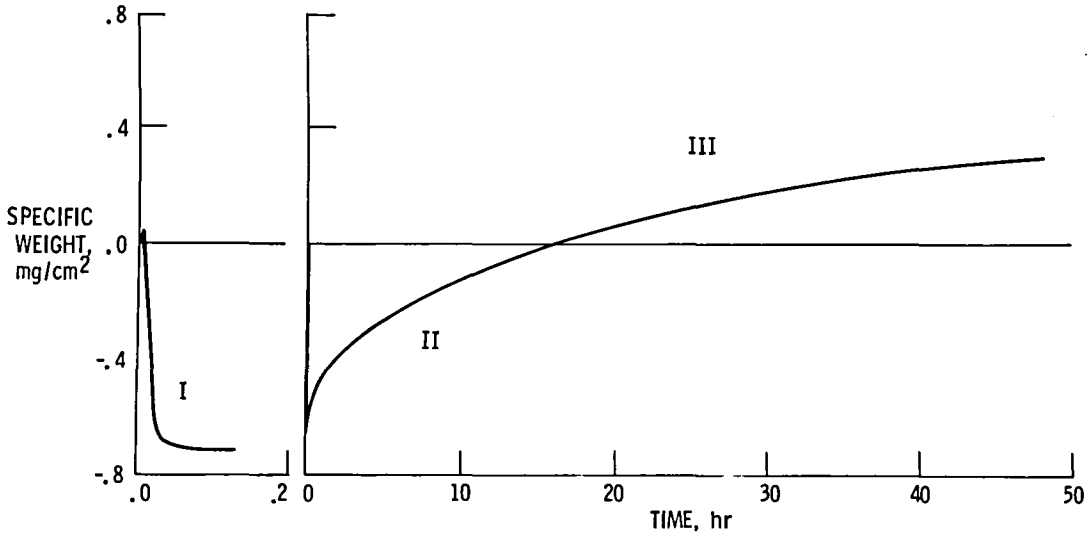
CS-86-1386

TGA - SINTERED α-SiC+Na_2CO_3/.1CO_2-O_2-1000 °C

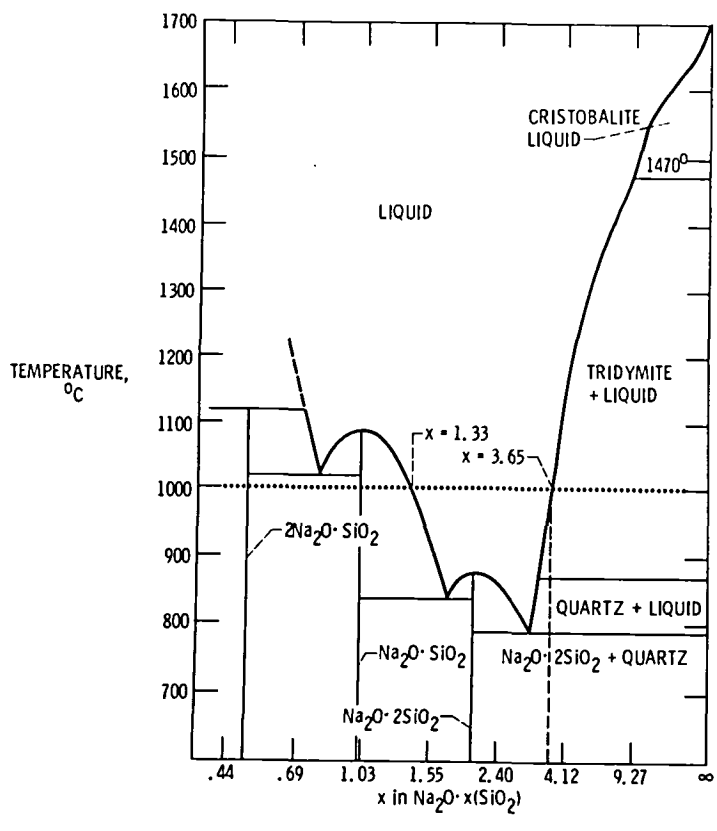


CS-86-1377

TGA - HIP'D RBSN + Na_2CO_3/O_2--1000 °C



CS-86-1378



CS-85-0793

MECHANISM OF CORROSION BY Na_2CO_3

I. DECOMPOSITION OF SALT AND SILICATE FORMATION

$$SiC + \frac{3}{2}O_2 = SiO_2 + CO$$

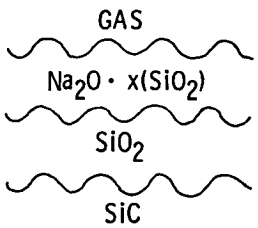
$$Na_2CO_3 + SiO_2 = Na_2O \cdot (SiO_2) + CO_2$$

II. MOVE TOWARD LIQUIDUS

$$SiC + \frac{3}{2}O_2 = SiO_2 + CO$$

$$Na_2O \cdot (SiO_2) + 2.65(SiO_2) = Na_2O \cdot 3.65(SiO_2)$$

III. GROWTH OF PROTECTIVE SiO_2 LAYER-SLOWING OF REACTION



CS-86-1380

Na_2CO_3 VERSUS Na_2SO_4/O_2

- $Na_2SO_4 = Na_2O + SO_3\uparrow$ BASIC MOLTEN SALT
- SiC - SIMILAR BEHAVIOR
- Si_3N_4 - Na_2SO_4/O_2 CORROSION IS SLOWER THAN Na_2CO_3/O_2
- IMPORTANT SYSTEM - CLOSE TO BURNER RIG

CS-86-1381

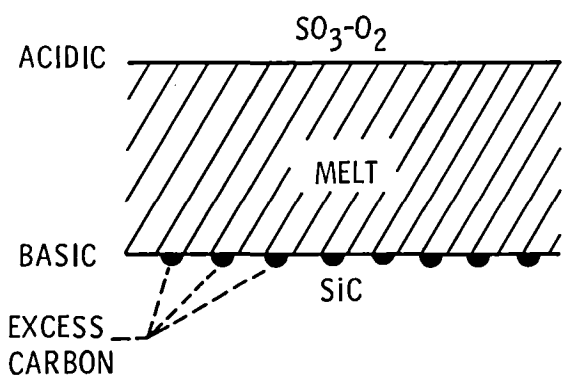
Na_2SO_4/SO_3 CASE

$Na_2SO_4 + SiO_2 = Na_2SiO_3 + SO_3$ $\quad \Delta G = +35$ k cal/mol

- $P_{SO_3} > 10^{-6}$ atm -- NO REACTION
- $Na_2SO_4/10^{-4}$ SO_3-O_2 DOES NOT ATTACK
  - QUARTZ
  - HOT PRESSED (Al_2O_3) SiC
  - SINGLE CRYSTAL SiC
  - PREOXIDIZED (1400 °C - 23 h) SINTERED SiC
- $Na_2SO_4/10^{-4}$ SO_3 - O_2 DRAMATICALLY ATTACKS AS-GROUND SINTERED SiC

CS-85-2269

BASIC/ACIDIC CHARACTER OF MELT



$Na_2SiO_3 + SO_3 = SiO_2 + Na_2SO_4$

$Na_2SO_4 + C + \frac{1}{2} O_2 = Na_2CO_3 + SO_2$

$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$

ESTABLISHES FLUXING CONDITION

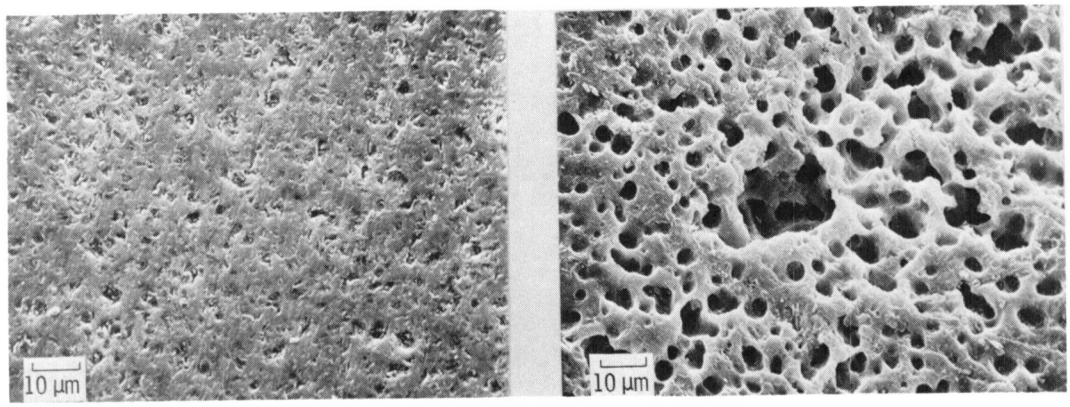
CS-85-2266

ATTACK OF CERAMIC SUBSTRATE

- HF REMOVES GLASSY PRODUCT LAYERS
  (CAUTION WITH Si_3N_4)
- ATTACK DOES NOT OCCUR BY EVEN RECESSION
- SiC - SEVERE PITTING ATTACK
  $Na_2CO_3 < Na_2SO_4/O_2 < Na_2SO_4/SO_3$
- Si_3N_4 - SEVERE GRAIN BOUNDARY ATTACK

CS-86-1385

CORROSION PITTING



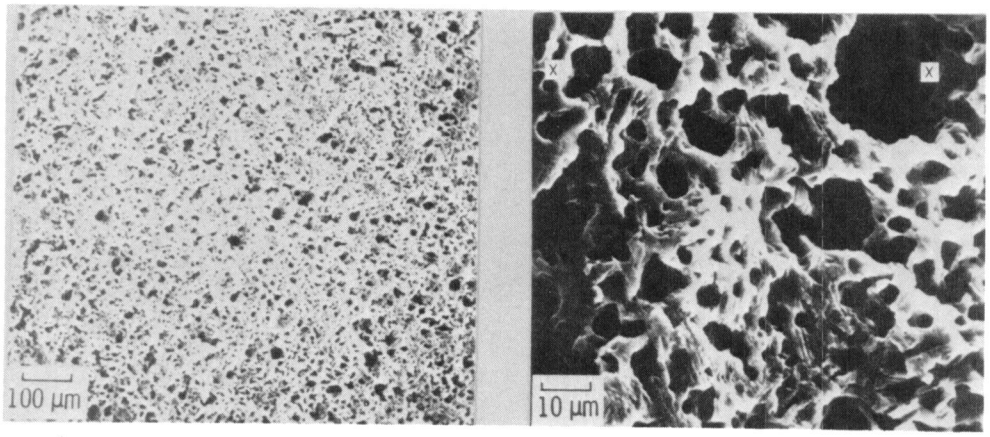
SINTERED α-SiC BEFORE CORROSION

SiC AFTER CORROSION
Na_2CO_3/CO_2 - 48 hrs - 1000 ^{o}C
PRODUCTS REMOVED WITH HF

CS-85-3407

PITTING ATTACK MORPHOLOGY AFTER Na_2SO_4/SO_3 CORROSION

SCALE REMOVED BY HF DISSOLUTION

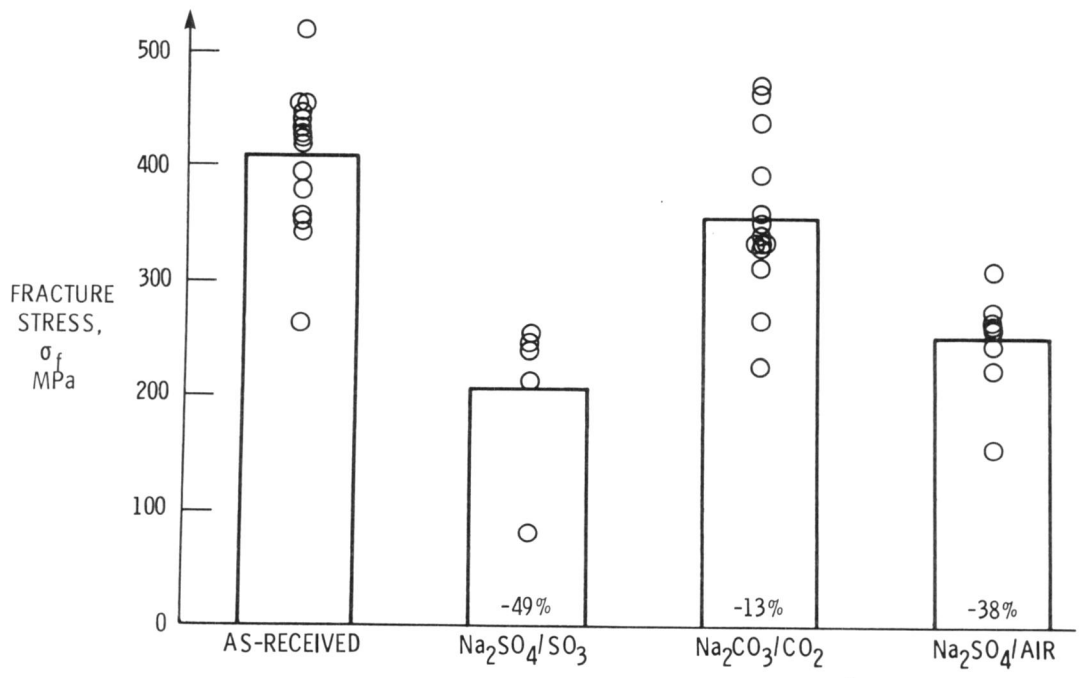


UNIFORM PITTING OBSERVED OVER LARGE AREAS

DETAIL OF (a) SHOWING HONEYCOMB PIT STRUCTURE

CS-85-2307

STRENGTH DEGRADATION OF α-SiC AFTER FURNACE CORROSION TESTING



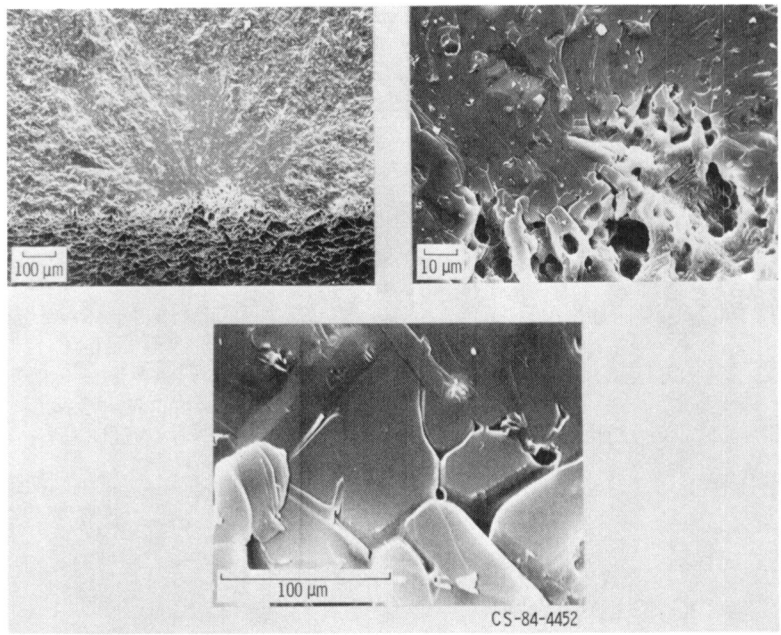
CS-85-2336

FRACTURE ORIGIN, PITTING, AND GRAIN BOUNDARY ATTACK AFTER Na_2SO_4/SO_3 CORROSION

SCALE REMOVED BY HF

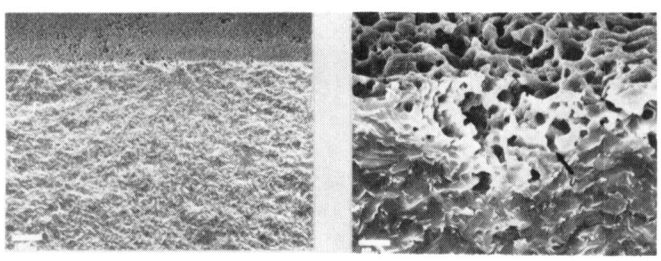
σ_f = 188 MPa

PIT DEPTH = 113 μm



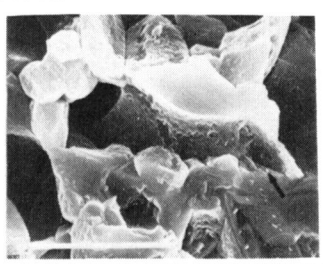
CORROSION PIT FRACTURE ORIGIN AFTER Na_2SO_4/AIR CORROSION

SCALE REMOVED BY HF DISSOLUTION; σ_f = 373 MPa, PIT DEPTH = 40 μm



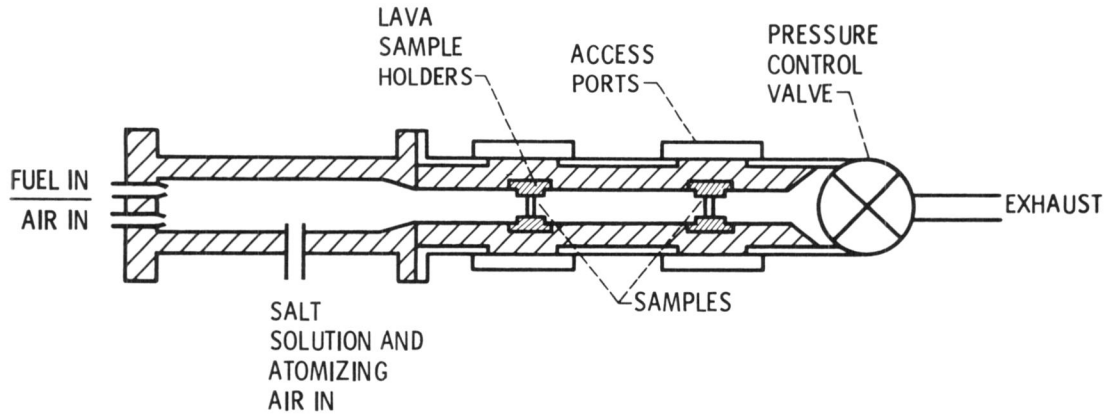
RADIAL CRACK LINES POINTING TO CORROSION PIT

INTERSECTION OF DEEPLY PITTED REGION WITH FRACTURE SURFACE



GRANULAR ATTACK MORPHOLOGY IN PIT

CS-85-2305

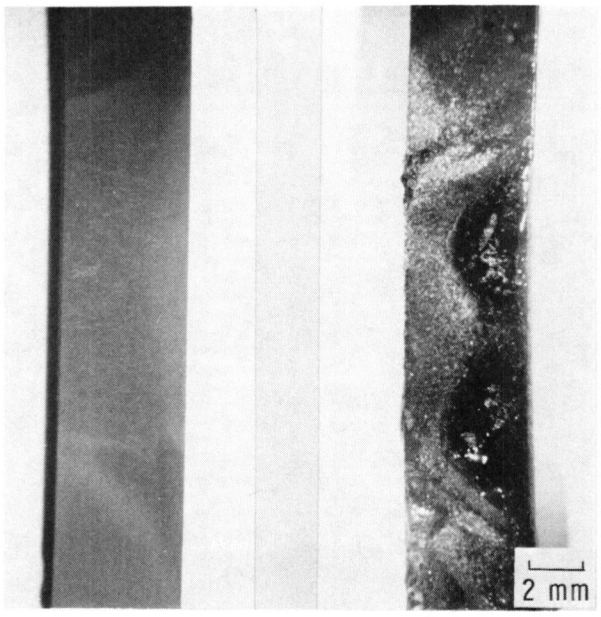


- PARALLEL TO Na_2SO_4/O_2 FURNACE STUDY
- CONTINUOUS SOURCE OF Na_2O
  -- CONTINUOUS $Na_2O \cdot x(SiO_2)$ FORMATION

OPERATING PARAMETERS
- $T = 990 \pm 10\ ^{o}C$
- JET A FUEL - 0.05% S
- 4 ppm Na AS NaCl
- FLOW VELOCITY - 310 ft/sec

CS-86-1376

BURNER RIG TESTS OF α-SiC AT 1000 °C



NO SALT
46 hr

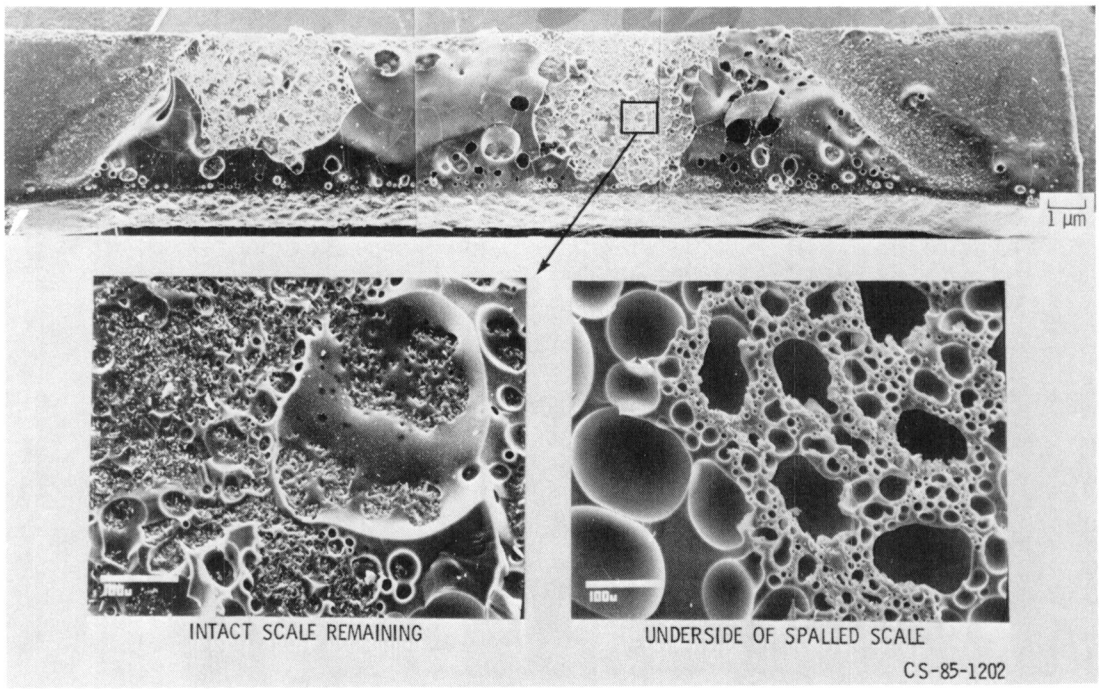
4 ppm Na
13.5 hr

AIR FLOW →

CS-85-1205

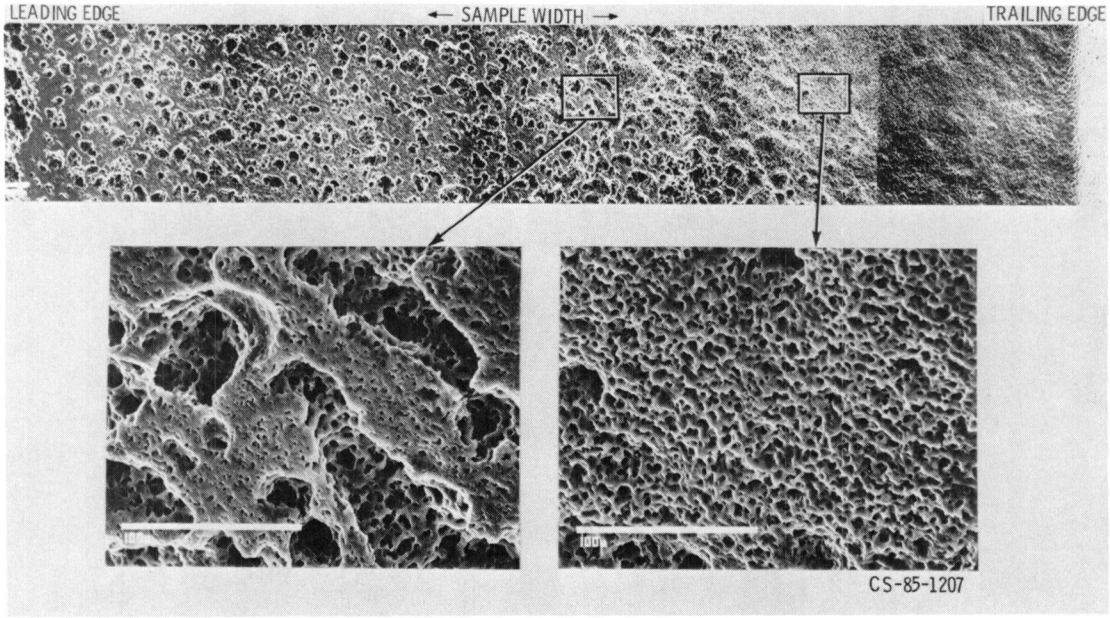
EXTENSIVE BUBBLE FORMATION IN BURNER RIG SAMPLES

MECHANICAL SCALE REMOVAL

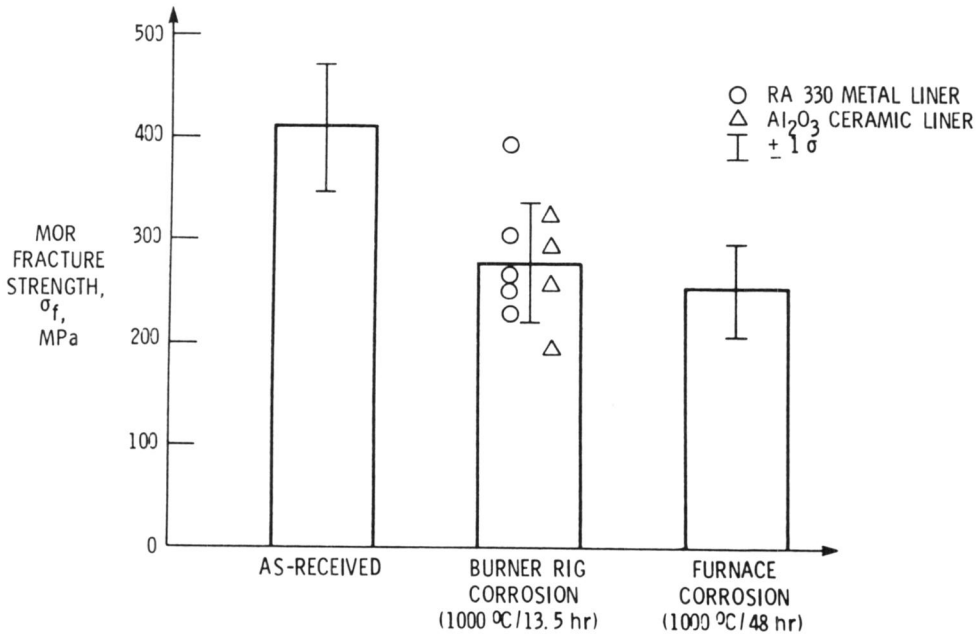


α-SiC PITTING MORPHOLOGY CAUSED BY BURNER RIG CORROSION

SCALE REMOVED BY HF DISSOLUTION

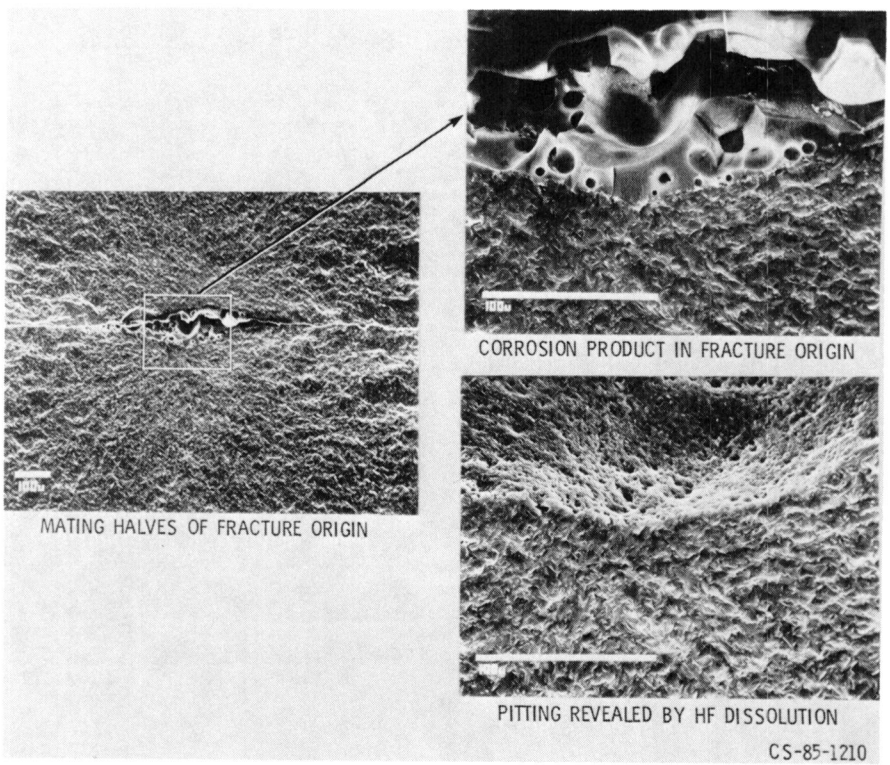


EFFECT OF BURNER RIG HOT CORROSION ON ROOM TEMPERATURE α-SiC STRENGTH



CS-85-1324

FRACTURE ORIGIN OF BURNER RIG CORROSION SPECIMEN



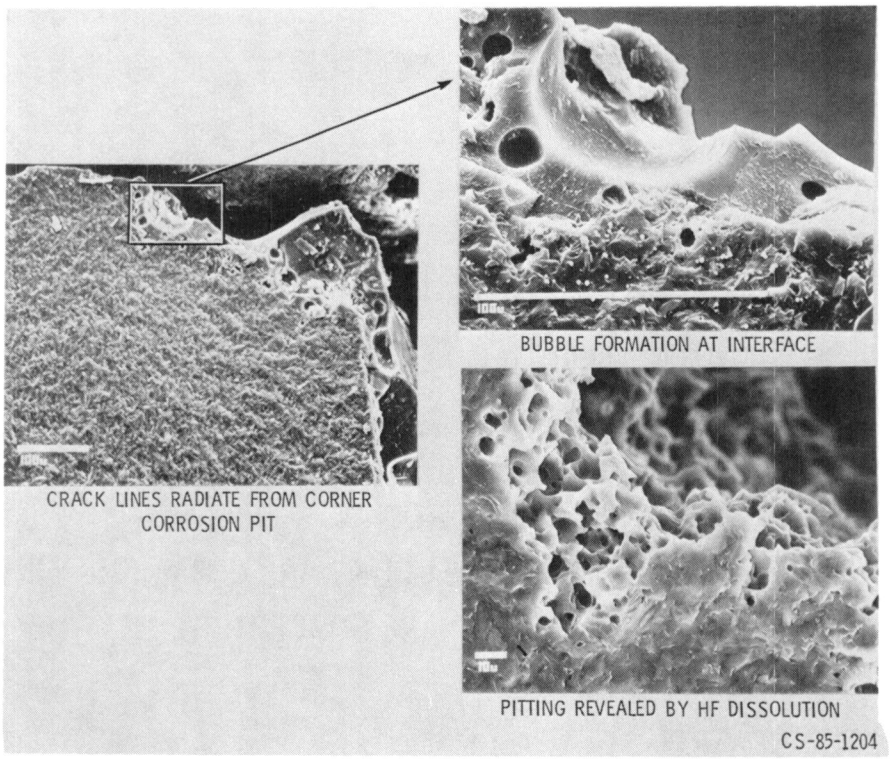
MATING HALVES OF FRACTURE ORIGIN

CORROSION PRODUCT IN FRACTURE ORIGIN

PITTING REVEALED BY HF DISSOLUTION

CS-85-1210

FRACTURE ORIGIN OF BURNER RIG CORROSION SPECIMEN



SUMMARY

LABORATORY STUDIES

- BASIC MOLTEN SALTS
  SiO_2 FORMATION AND DISSOLUTION TO LIQUIDUS
- ACIDIC MOLTEN SALTS
  NO ATTACK, UNLESS BASIC CONDITIONS AT MELT BOTTOM

BURNER RIG

- PARALLEL TO Na_2SO_4/O_2 - BASIC SALT ATTACK
- CONTINUOUS $Na_2O \cdot x(SiO_2)$ FORMATION

ATTACK OF CERAMICS

- SiC -- SEVERE PITTING -- UP TO 50% STRENGTH REDUCTION
- Si_3N_4 - SEVERE GRAIN BOUNDARY ATTACK -- WORK IN PROGRESS

SUMMARY AND CONTROL STRATEGIES

- MOLTEN SALT CORROSION
  - CAN BE CATASTROPHIC
  - ENGINEERS MUST BE AWARE CERAMICS, LIKE SUPERALLOYS, ARE SUSCEPTIBLE
- CONTROL STRATEGIES
  - WORK OUTSIDE SALT DEPOSITION REGIME
  - MAKE SALTS ACIDIC
  - COATINGS; MODIFY SiO_2 LAYER

CS-86-1390

THERMAL CYCLIC DURABILITY TESTING OF CERAMIC MATERIALS FOR TURBINE ENGINES

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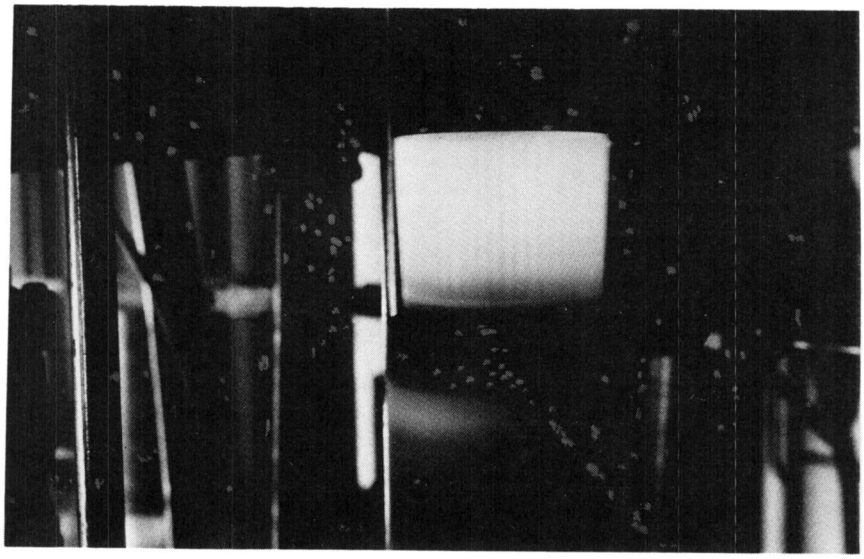
Phoenix, Arizona 85010

The thermal cyclic durability of commercial ceramic materials for turbine engines has been under evaluation since 1978. Ceramic materials are exposed to cyclic diesel-fired burner exhaust at either 1204 or 1371C (2200 or 2500F) for up to 3500 hours. The test conditions are selected to simulate the environment experienced by the hot flow path components in an automotive gas turbine engine. The silicon nitride and silicon carbide materials tested are the same ceramic materials currently used on the AGT100 and AGT101 ceramic turbine engine programs.

This work was performed under the NASA funded program, 3500-Hour Durability Testing of Commercial Ceramic Materials, Contract DEN3-27.

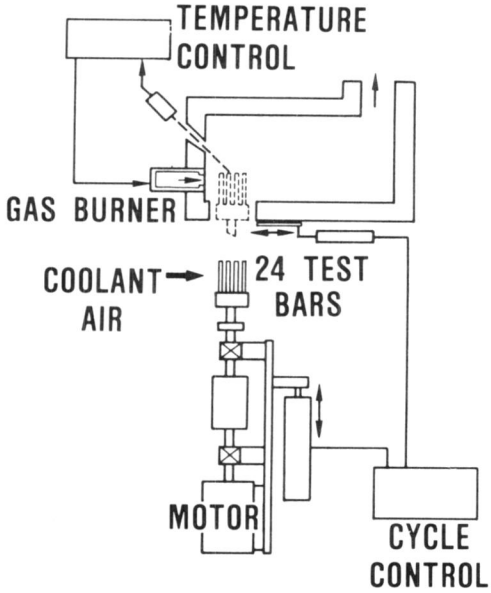
THERMAL CYCLIC DURABILITY TESTING OF CERAMIC MATERIALS FOR TURBINE ENGINES



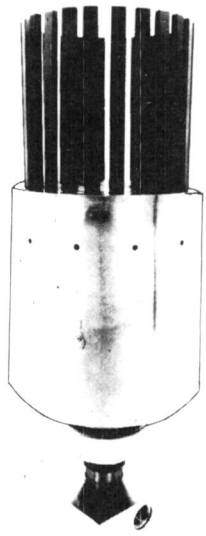
3500-HOUR DURABILITY TESTING OF COMMERCIAL CERAMIC MATERIALS

- OBJECTIVE
  - DETERMINE LONG-TERM DURABILITY OF CERAMIC GAS TURBINE ENGINE MATERIALS
- APPROACH
  - CYCLE CERAMIC TEST BARS FROM HIGH TEMPERATURE BURNER EXHAUST TO COLD AIR
  - MONITOR CHANGES IN STRENGTH, WEIGHT, AND DIMENSIONS WITH EXPOSURE TIME AND COMPARE TO BASELINE PROPERTIES
  - TESTING IS TERMINATED WHEN THE STRENGTH IS REDUCED TO 50 PERCENT OF THE BASELINE STRENGTH
- BENEFITS
  - IDENTIFIES CERAMIC MATERIALS CAPABLE OF LONG-TERM USE IN GAS TURBINE ENGINE
  - PROVIDES DIRECT COMPARISON OF NEW CERAMICS WITH MATERIALS PREVIOUSLY TESTED IN THIS CONTINUING PROGRAM

NASA/GARRETT FACILITY DEVELOPED FOR 1371C (2500F) CYCLIC DURABILITY TESTING



CERAMIC TEST BAR DURABILITY TEST FACILITY



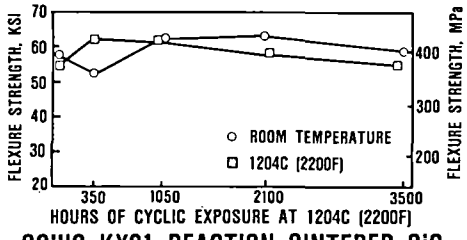
AIR COOLED CERAMIC TEST BAR HOLDER

G4-0255-12

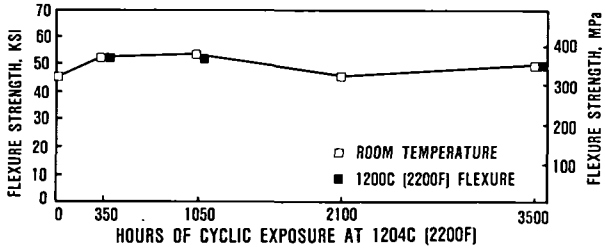
A VARIETY OF CERAMICS HAVE BEEN DURABILITY TESTED

MATERIAL	TEMP, C (F)	DURABILITY, HOURS
SOHIO SINTERED ALPHA SILICON CARBIDE (SASC)	1204 (2200)	3500
SOHIO REACTION SINTERED SILICON CARBIDE (RSSC)	1204 (2200)	3500
ACC RBN 101 REACTION BONDED SILICON NITRIDE (RBSN)	1204 (2200)	2100
REFEL SILICONIZED SILICON CARBIDE (SiSC)	1204 (2200)	2100
NGK SN-50 SINTERED SILICON NITRIDE (SSN)	1204 (2200)	<350
GTE AY6 SSN	1204 (2200)	<350
TOSHIBA SSN	1204 (2200)	<350
ACC SSN	1204 (2200)	<350
NORTON NCX 34 HOT PRESSED SILICON NITRIDE (HPSN)	1204 (2200)	<100
SOHIO SASC	1371 (2500)	3500
ACC RBSN	1371 (2500)	2100
REFEL SiSC	1371 (2500)	<350

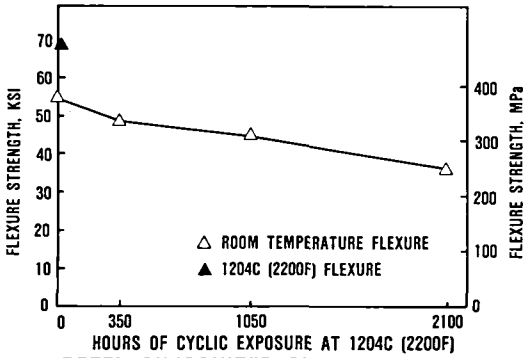
SEVERAL CERAMIC MATERIALS DEMONSTRATE ACCEPTABLE PERFORMANCE AT 1204C (2200F)



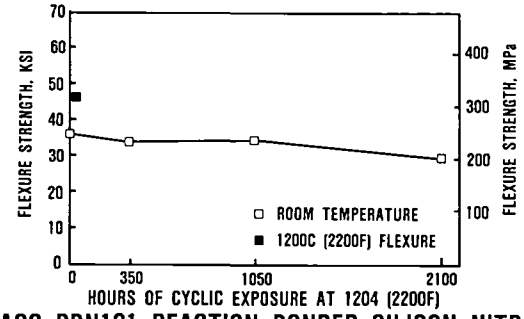
SOHIO KX01 REACTION SINTERED SiC



SOHIO SINTERED ALPHA SILICON CARBIDE



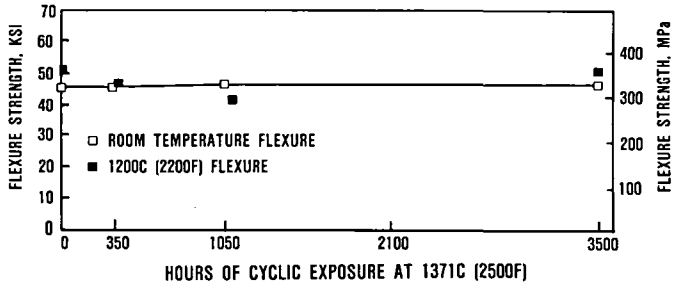
REFEL SILICONIZED SILICON CARBIDE



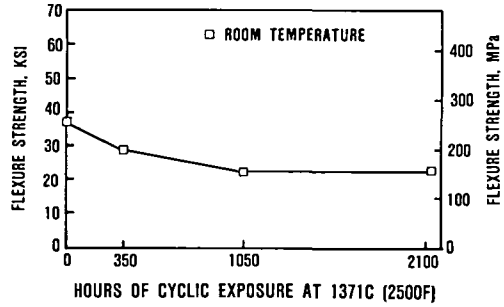
ACC RBN101 REACTION BONDED SILICON NITRIDE

TEST RESULTS SHOW CERAMIC DURABILITY AT 1371C (2500F)

SOHIO SINTERED ALPHA SILICON CARBIDE



ACC RBN101 REACTION BONDED SILICON NITRIDE



NEW MATERIALS ARE TESTED AS THEY BECOME AVAILABLE

- KYOCERA SC201 SINTERED SILICON CARBIDE (SSC) — DURABILITY TESTING IN PROGRESS
- SOHIO SASC (INJECTION MOLDED, AS-FIRED SURFACES) — DURABILITY TESTING IN PROGRESS
- GE β SSC — BASELINE TESTING COMPLETE
- CORNING LAS — BASELINE TESTING COMPLETE
- NGK SN-82 SSN — BASELINE TESTING COMPLETE
- ACC CODE 2 SSN — TO BE PROCURED
- KYOCERA SN 250M OR 270M SSN — TO BE PROCURED

BASELINE STRENGTH OF KYOCERA SINTERED SILICON CARBIDE HAS BEEN DETERMINED

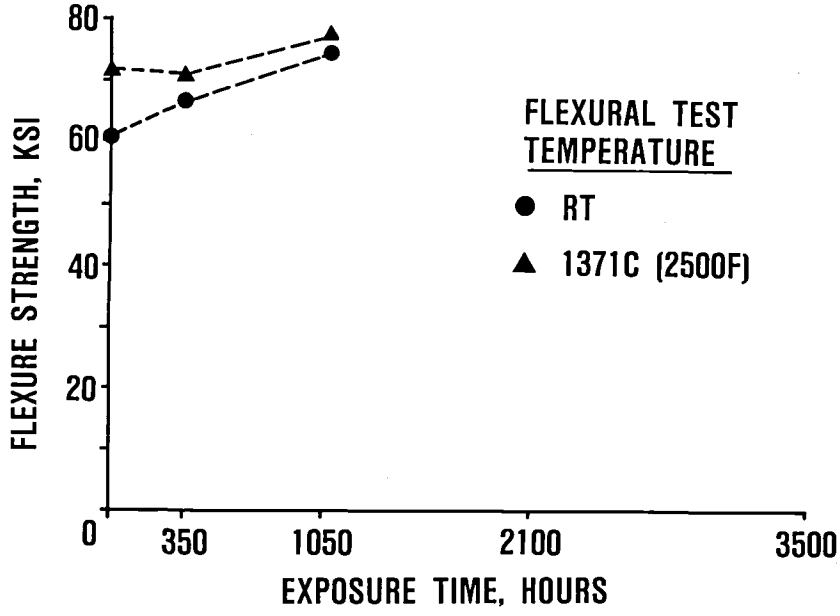
MATERIAL: KYOCERA SC201

CONDITION: AS-FIRED TEST BARS

	ROOM TEMPERATURE	1204C (2200F)	1371C (2500F)
MEAN STRENGTH, KSI (12 DATA POINTS)	61.9	66.2	71.3
STANDARD DEVIATION, KSI	11.4	8.2	8.8

CYCLIC EXPOSURE TESTING IS BEING CONDUCTED AT 1371C (2500F)

KYOCERA SC201 HAS UNDERGONE 1050 HOURS OF CYCLIC EXPOSURE TO 1371C (2500F)



BASELINE STRENGTH OF SOHIO INJECTION MOLDED SINTERED SiC HAS BEEN DETERMINED

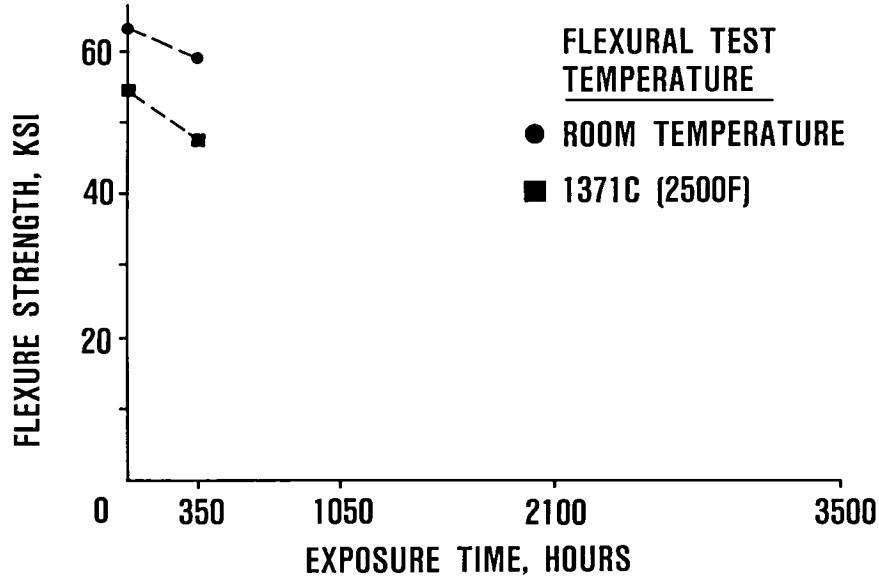
MATERIAL: SOHIO SASC

CONDITION: AS-FIRED TEST BARS

	ROOM TEMPERATURE	1204C (2200F)
MEAN STRENGTH, KSI (12 DATA POINTS)	63.5	60.7
STANDARD DEVIATION, KSI	9.2	7.6

CYCLIC EXPOSURE TESTING IS BEING CONDUCTED AT 1371C (2500F)

SOHIO INJECTION MOLDED SASC HAS UNDERGONE 350 HOURS OF CYCLIC EXPOSURE TO 1371C (2500F)



BASELINE STRENGTH OF GE β SILICON CARBIDE HAS BEEN DETERMINED

MATERIAL: GE β SiC

CONDITION: AS-FIRED TEST BARS

	ROOM TEMPERATURE	1371C (2500F)
MEAN STRENGTH, KSI (12 DATA POINTS)	61.4	61.2
STANDARD DEVIATION, KSI	4.6	8.9

CYCLIC EXPOSURE TESTING TO BE CONDUCTED AT 1371C (2500F)

BASELINE STRENGTH OF NGK SINTERED SILICON NITRIDE HAS BEEN DETERMINED

MATERIAL: NGK SN-82

CONDITION: AS-FIRED TEST BARS

	ROOM TEMPERATURE	982C (1800F)	1204C (2200F)
MEAN STRENGTH, KSI (12 DATA POINTS)	120.4	103.9	97.3
STANDARD DEVIATION, KSI	14.0	9.2	5.5

CYCLIC EXPOSURE TESTING TO BE CONDUCTED AT 1204C (2200F)

RESULTS

- SOHIO SASC (ISOPRESSED, MACHINED SURFACES) EXPERIENCES NO NO STRENGTH DEGRADATION AFTER 3500 HOURS OF CYCLIC EXPOSURE AT 1371C (2500F)
- SOHIO RSSC EXPERIENCES NO STRENGTH DEGRADATION AFTER 3500 HOURS OF CYCLIC EXPOSURE AT 1204C (2200F)
- ACC RBSN EXPERIENCES A 20-PERCENT STRENGTH REDUCTION AT 1204C (2200F) AFTER 2100 HOURS OF EXPOSURE AND A 20-PERCENT STRENGTH REDUCTION AFTER 350 HOURS AT 1371C (2500F)
- ALL SSN MATERIALS TESTED TO DATE (NGK SN-50, ACC CODE 2, GTE AY6, TOSHIBA SSN) EITHER EXHIBITED LOW BASELINE FLEXURE STRENGTHS AND/OR SHOWED >50-PERCENT STRENGTH DEGRADATION DURING THE FIRST 350 HOURS OF CYCLIC EXPOSURE AT 1204C (2200F)

BASELINE FLEXURE STRENGTH AND CYCLIC DURABILITY TESTING IS SCHEDULED FOR 1986-1987

- CYCLIC EXPOSURE TESTING IS CURRENTLY BEING CONDUCTED ON INJECTION MOLDED SOHIO SASC WITH AS-FIRED SURFACES AND KYOCERA SSC WITH AS-FIRED SURFACES AT 1371C (2500F)
- CYCLIC EXPOSURE TESTING OF GE β SSC, CORNING LAS, NGK SN-82 SSN AND ACC CODE 2 SSN WILL BE CONDUCTED DURING 1986-1987
- KYOCERA SN-250M OR 270M WILL BE PROCURED FOR BASELINE AND EXPOSURE TESTING DURING 1986-1987

FRACTOGRAPHIC AND MICROSTRUCTURAL EVALUATION OF 3500-HOUR DURABILITY SPECIMENS

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NASA Lewis Research Center has since 1978 contracted with Garrett Turbine Engine Company to conduct long-term durability testing of candidate ceramic materials for advanced gas turbine applications. Specimens of the materials are exposed to combustion atmospheres under temperature cyclic conditions for times up to 3500 hours and at peak temperatures of 1200 and 1370 C. The specimen strengths after exposure are measured at room temperature and at 1200 C. In addition, a number of physical measurements are taken, however no provision is made in the contract for microstructural examination of the specimens.

The work under this project covers examination of three materials, (1) sintered alpha silicon carbide manufactured by Carborundum Co., (2) sintered silicon nitride, manufactured by Toshiba, and (3) reaction bonded silicon nitride, grade RBN-104, manufactured by Airesearch Casting Company. The work required the development of sample preparation techniques to provide high quality thin-section specimens which can be examined by transmitted light or thinned using an ion mill for subsequent TEM examination.

Specimen preparation techniques and the results of optical and electron microscopic examination of the reaction interfaces of the selected specimens are presented and discussed.

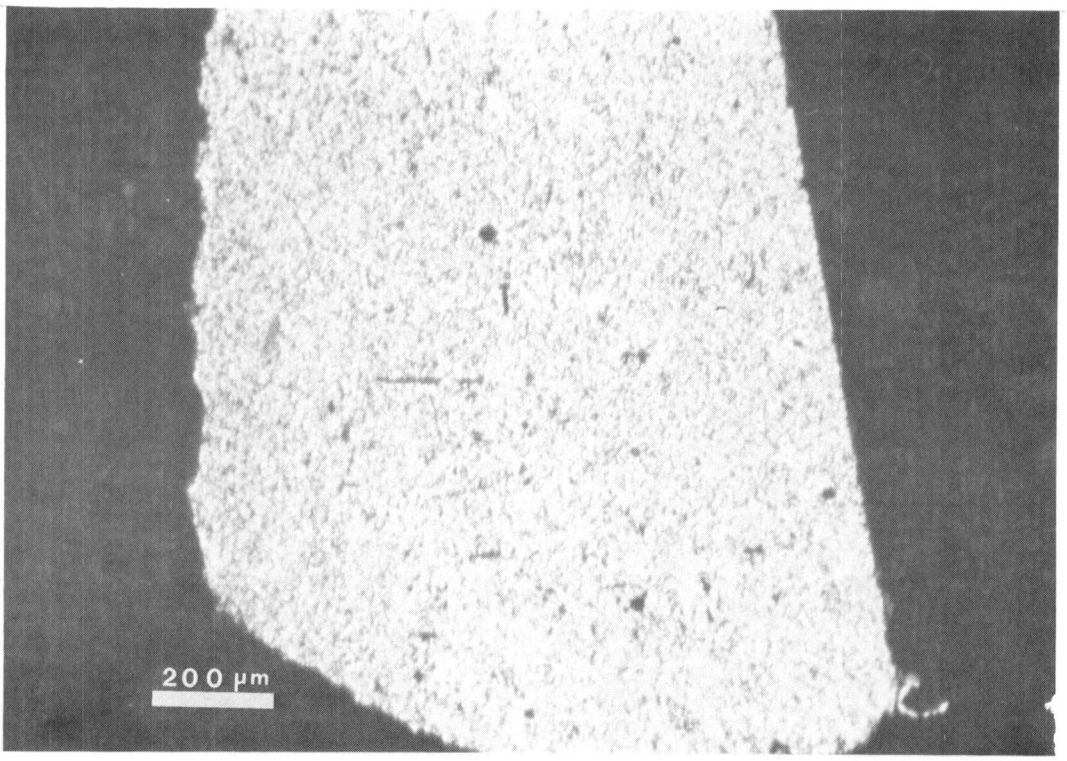

Figure 1. - Baseline SASC; crossed Nichols. 95X

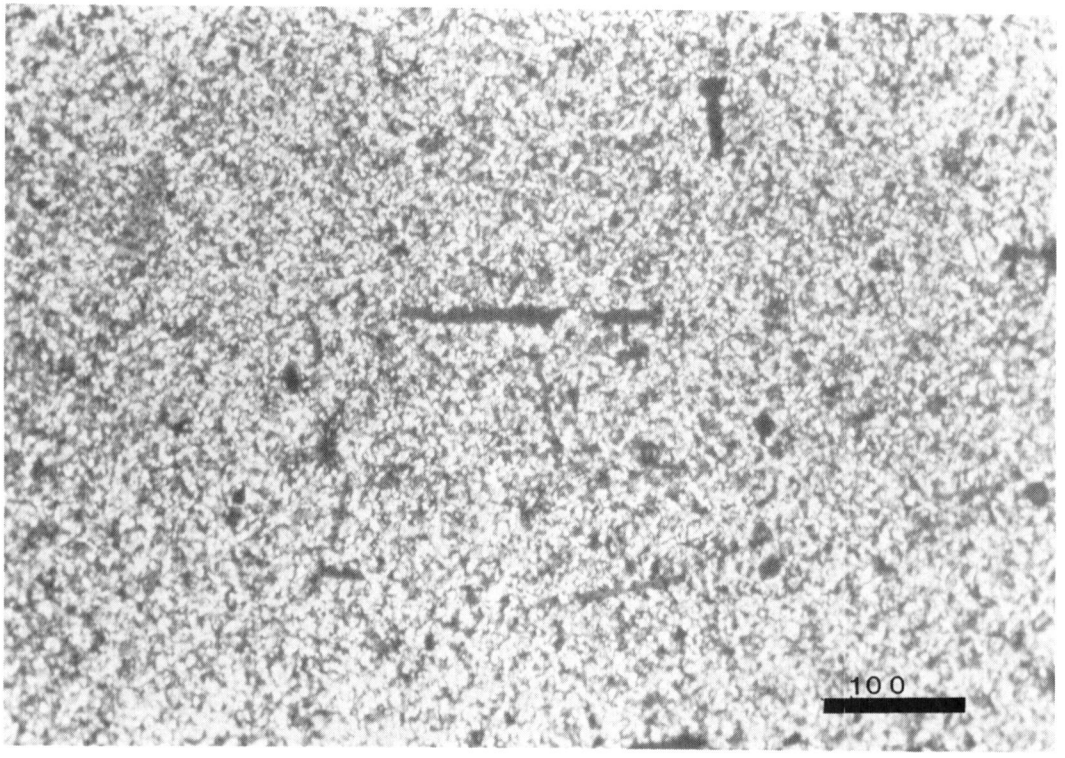

Figure 2. - Baseline SASC; crossed Nichols. 240X.

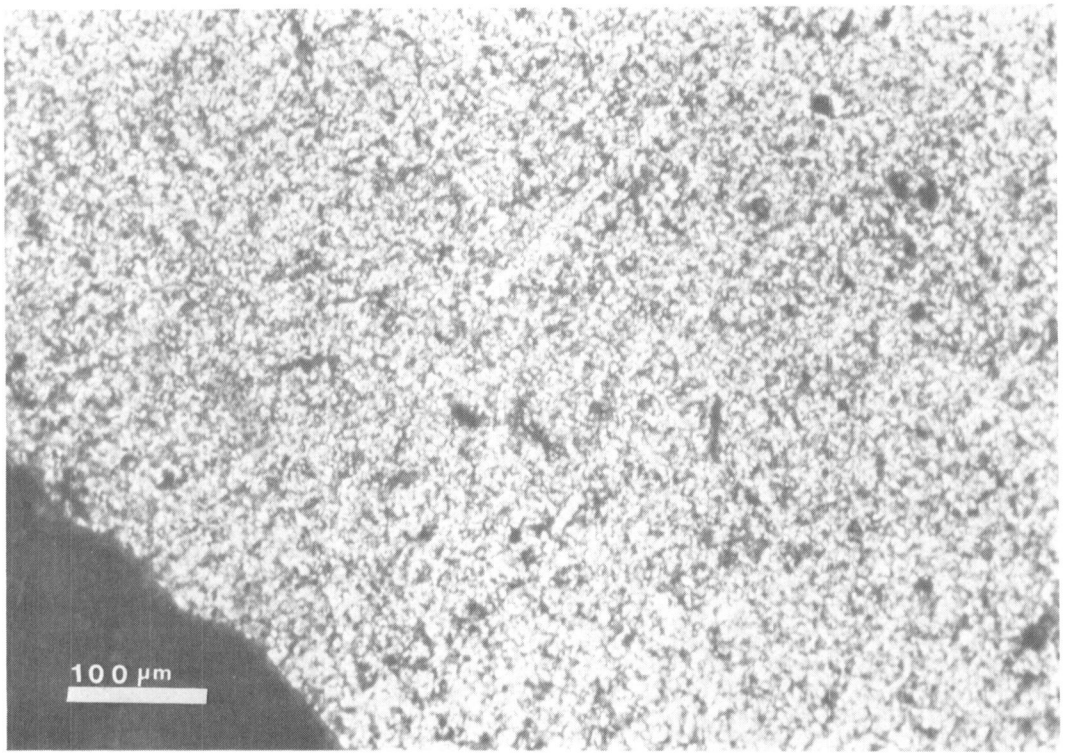

Figure 3. - Same field as fig.2; crossed Nichols, rotated 45°. 240X.

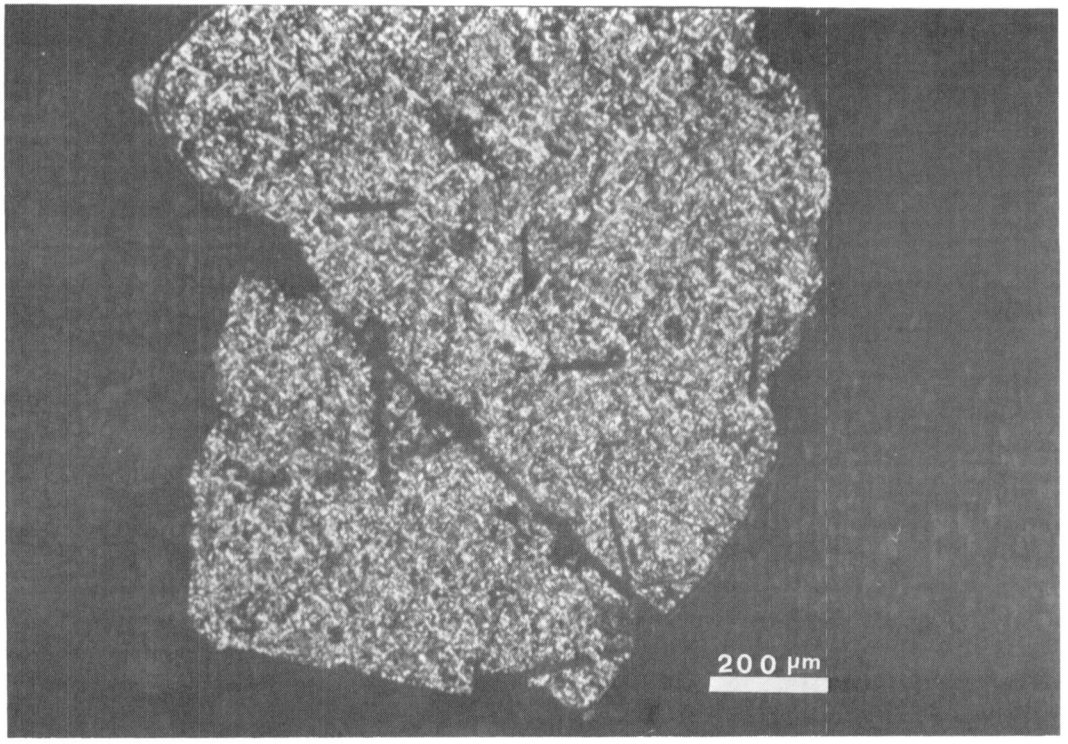

Figure 4. - SASC; 2100-hr exposure at 1370 °C; crossed Nichols. 95X.

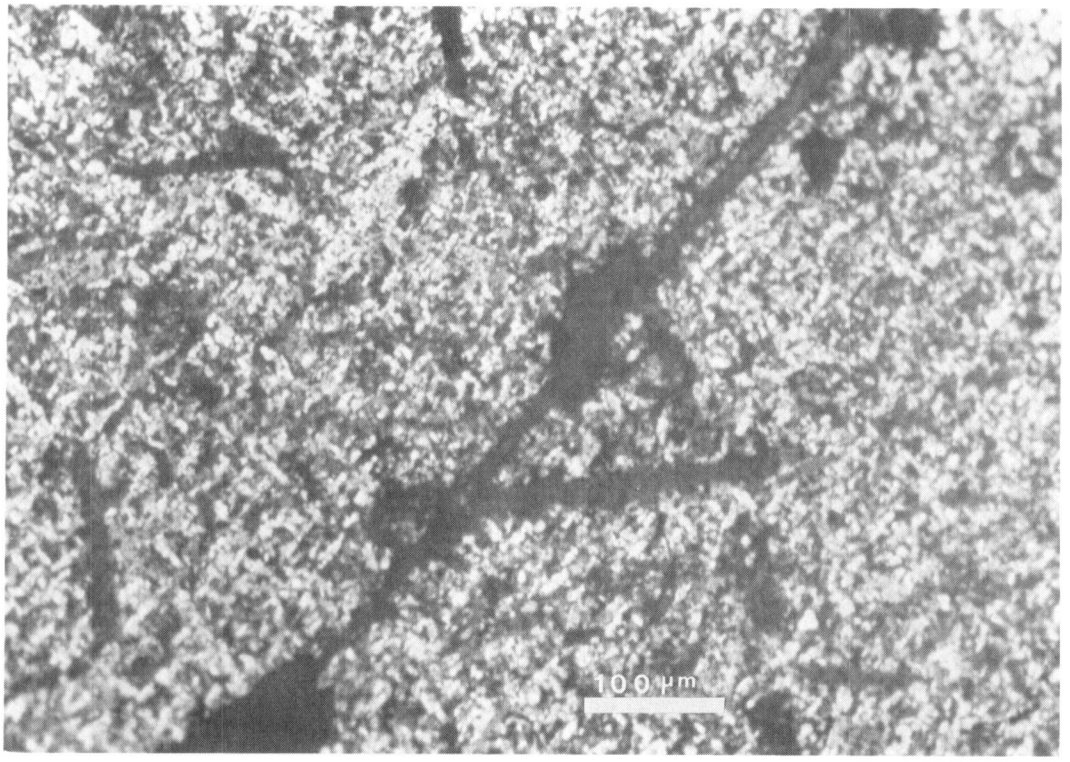

Figure 5. - Same field as fig. 4. 240X.

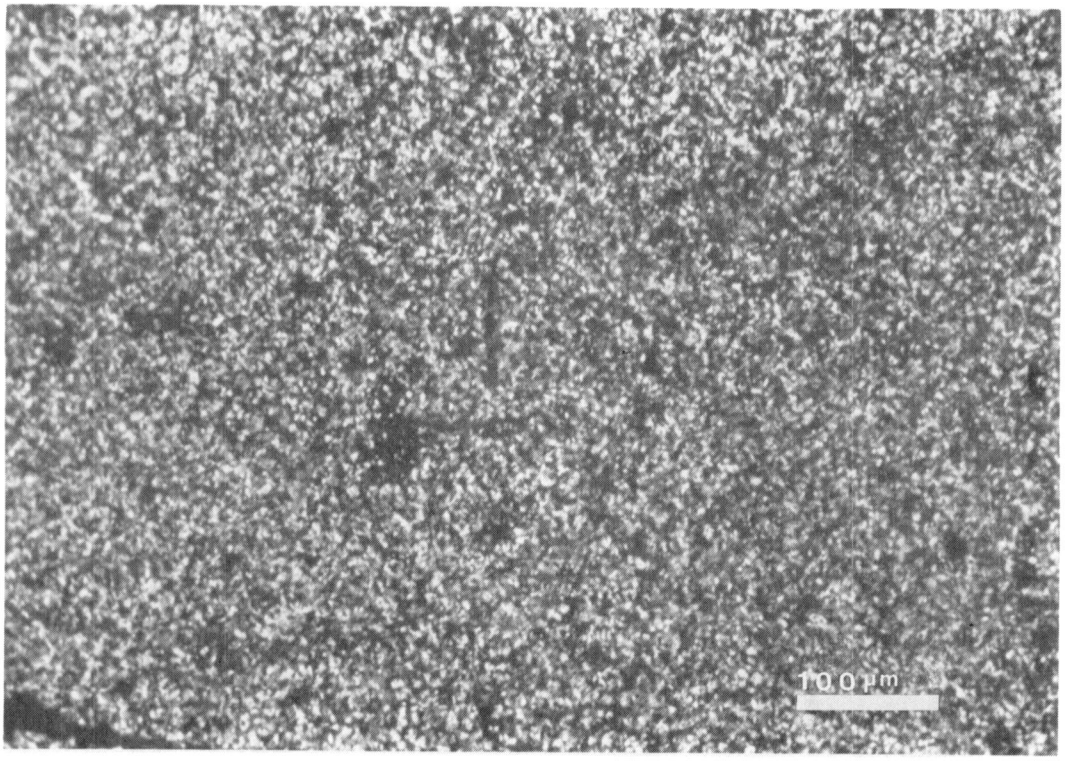

Figure 6. - SASC; 3500-hr exposure at 1370 °C; crossed Nichols. 240X.

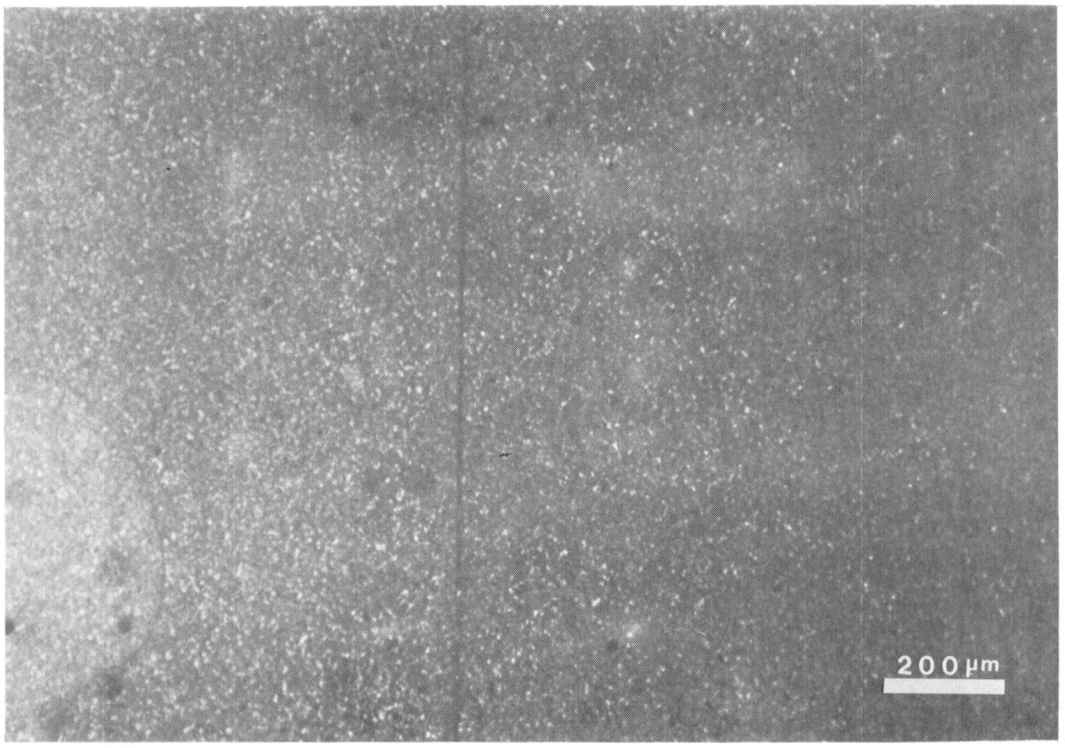

Figure 7. - Baseline Toshiba SSN; crossed Nichols. 95X.

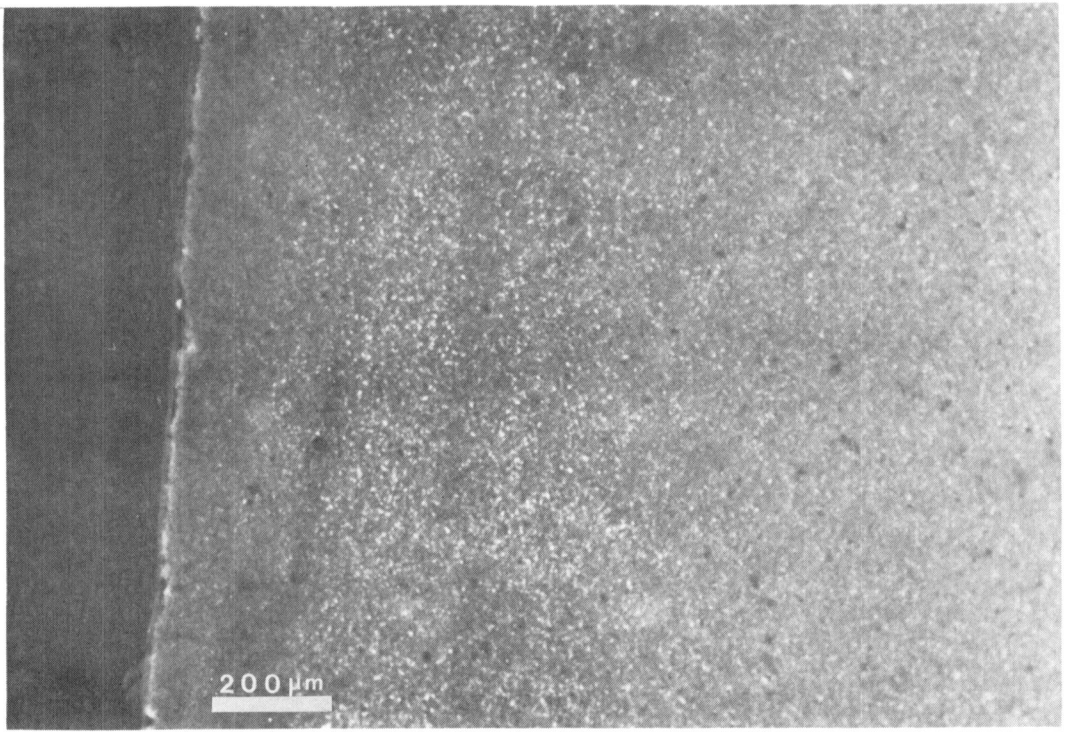

Figure 8. - Toshiba SSN; 350-hr exposure at 1205 °C; crossed Nichols. 95X.

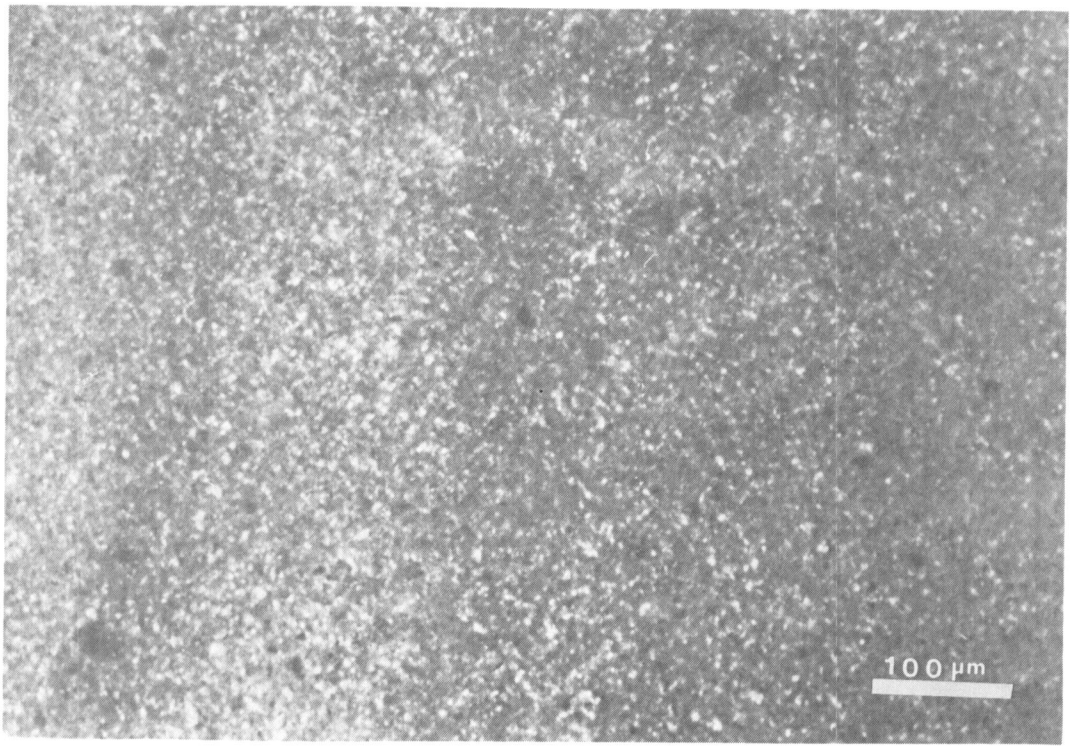

Figure 9. - Same specimen as fig. 8; field near interface; crossed Nichols. 240X

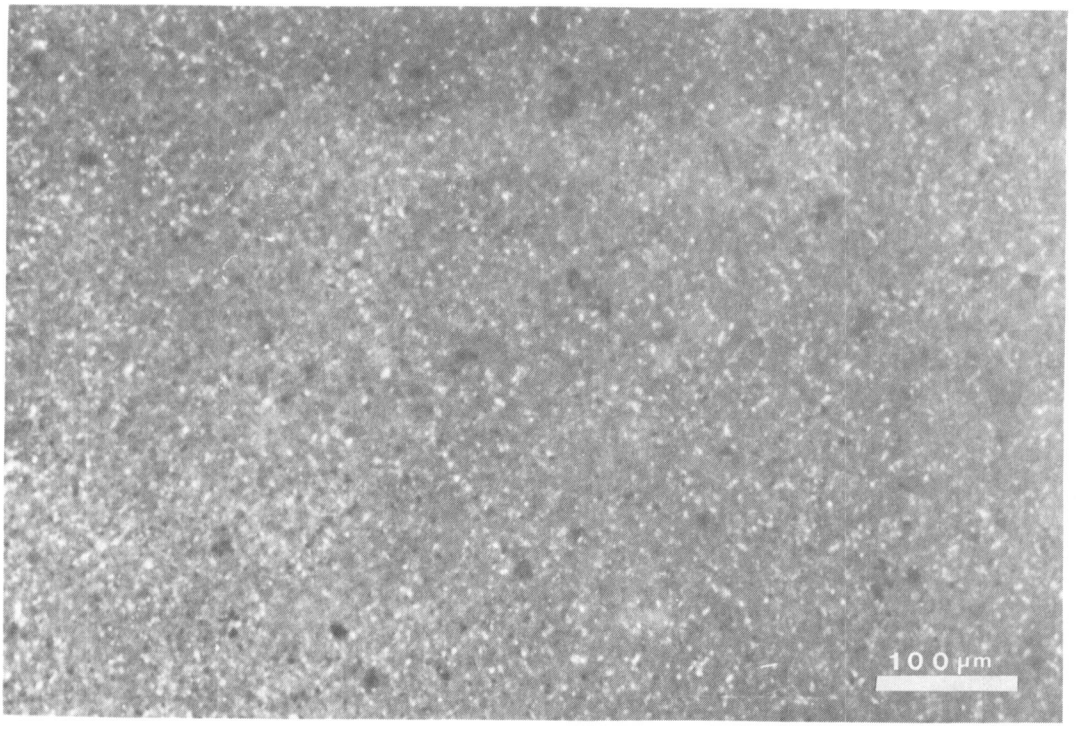

Figure 10. - Same specimen as fig 8; field far from interface; crossed Nichols. 240X.

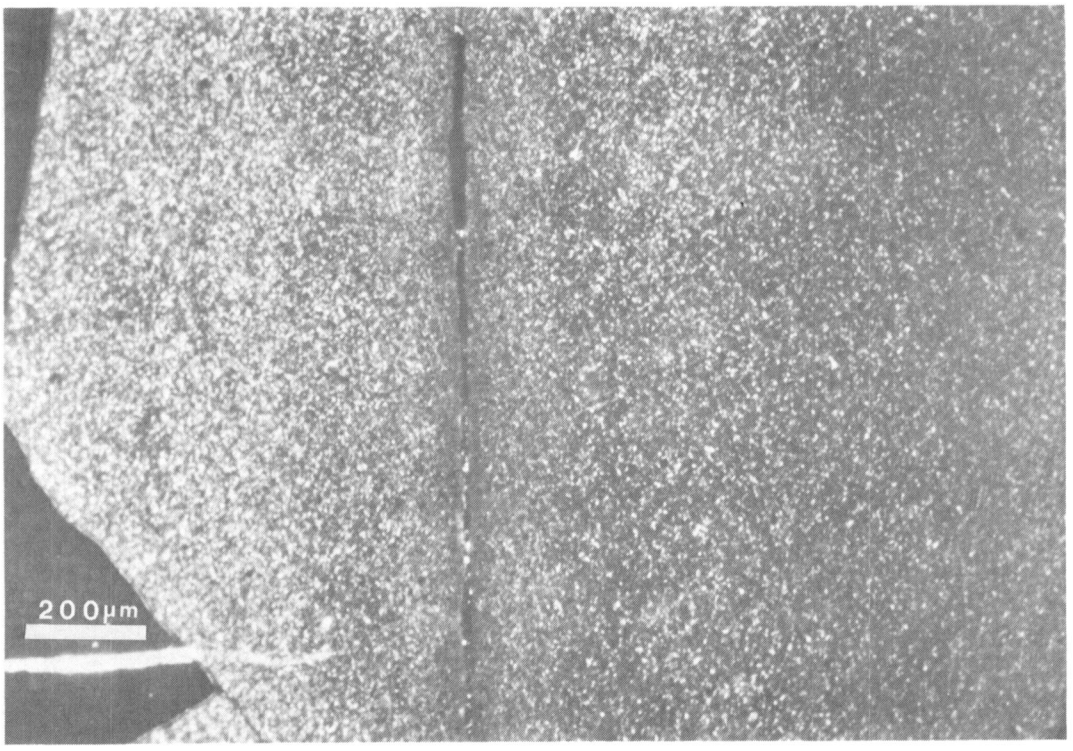

Figure 11. - Toshiba SSN; 700-hr exposure; crossed Nichols. 95X.

CERAMIC MATRIX COMPOSITES

James A. DiCarlo
NASA Lewis Research Center
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An overview is presented covering NASA Lewis research efforts aimed at materials and processing development for structually reliable fiber-reinforced ceramic matrix composites (FRC). With the primary goal of developing technology for strong, tough Si-based FRC with use-temperatures above 1400°C, guidelines for optimum material properties and current problems in achieving these properties are discussed. Brief descriptions of particular research projects directed toward solving these problems are presented. Particular emphasis is placed on those efforts addressing the critical need of developing high performance SiC fibers with stability above 1400°C and with proper coatings for optimum composite structural performance. Based on current results for fiber and matrix development, concluding remarks are made concerning future directions for NASA Lewis FRC studies.

CERAMIC MATRIX COMPOSITES

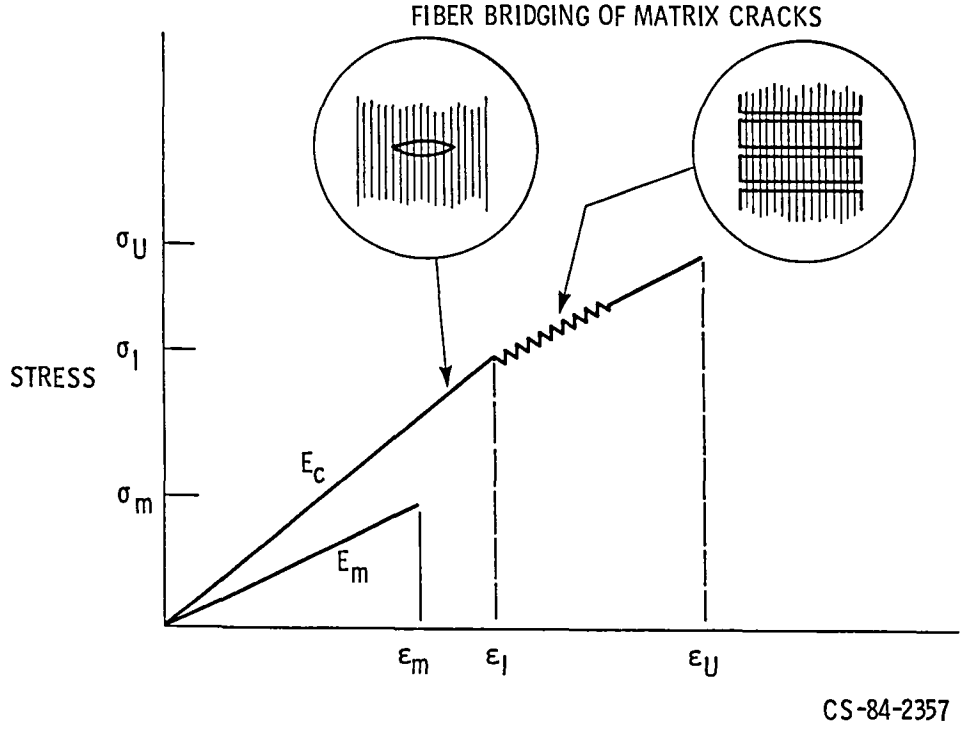
BY

J. DiCARLO
DEPUTY CHIEF, CERAMICS BRANCH

OBJECTIVE: TECHNOLOGY DEVELOPMENT FOR FABRICATION OF STRONG, TOUGH, AND RELIABLE CERAMIC COMPOSITES FOR AEROSPACE STRUCTURAL APPLICATIONS TO 1400 ^{o}C AND ABOVE

PRIMARY APPROACH: FIBER REINFORCED CERAMICS (FRC) - REINFORCEMENT OF Si-BASED CERAMIC MATRICES WITH CONTINUOUS HIGH PERFORMANCE CERAMIC FIBERS

FRC DEFORMATION AND FRACTURE



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STRUCTURAL ADVANTAGES OF FIBER REINFORCED CERAMICS

- IMPROVED STIFFNESS
  - MATRIX FRACTURE STRENGTH
  - MATRIX FRACTURE STRAIN
  - FRACTURE TOUGHNESS
  - THERMAL SHOCK
- * METAL-LIKE STRESS-STRAIN BEHAVIOR
- * ULTIMATE FAILURE INDEPENDENT OF MATRIX FRACTURE
- * NONCATASTROPHIC MATERIAL FAILURE

*AVAILABLE ONLY FOR HIGH ASPECT RATIO REINFORCEMENT

FRC - KEY TECHNICAL ISSUES

I. FABRICATION APPROACH FOR HIGH FRC STRENGTH
- PREPARATION OF OPTIMUM MATRIX PRECURSORS
- UNIFORM PRECURSOR INFILTRATION INTO FIBER ARRAY
- MATRIX CONSOLIDATION AND DENSIFICATION WITHOUT
  - FIBER STRENGTH DEGRADATION
  - LARGE SHRINKAGE CRACKS OR POROSITY
  - NONUNIFORM FIBER DISTRIBUTION

II. AVAILABILITY OF HIGH PERFORMANCE CERAMIC FIBERS
- HIGH STRENGTH AND STIFFNESS
- THERMAL STABILITY ABOVE 1200 ^{o}C
- SMALL DIAMETER

III. FIBER COATINGS
- FIBER STRENGTH RETENTION UNDER FRC PROCESSING AND USE
- OPTIMUM FOR COMPOSITE TOUGHNESS AND OFF-AXIS STRENGTH

FRC - CURRENT NASA LEWIS PROGRAMS

I. COMPOSITE FABRICATION

PROCESSING APPROACH	PRIMARY SYSTEM	KEY ISSUES
• REACTION-BONDED Si_3N_4 WITH CVD SiC FIBERS	SiC/RBSN	- STRENGTH AND TOUGHNESS GREATER THAN RBSN - THERMAL STABILITY TO 1400 °C
• CARBON MATRICES REACTION BONDED WITH SILICON	SiC/RBSC	- MATRIX MORPHOLOGY AND SILICONIZATION - FIBER DEGRADATION
• POLYMER-DERIVED PRECURSORS TO SiC AND Si_3N_4 MATRICES		- HIGH CHAR YIELD - INFILTRATION RHEOLOGY WITH CERAMIC FILLERS

FRC - CURRENT NASA LEWIS PROGRAMS

II. HIGH PERFORMANCE SiC FIBERS

• HIGH TEMPERATURE PROPERTIES OF COMMERCIAL SiC FIBERS	- FIBER PROCESSING APPROACH BEST SUITED FOR HIGH TEMPERATURE FRC
• POST PROCESSING OF NiCALON FIBERS AT HIGH PRESSURE	- POTENTIAL OF HIPPING FOR IMPROVING NiCALON THERMAL STABILITY

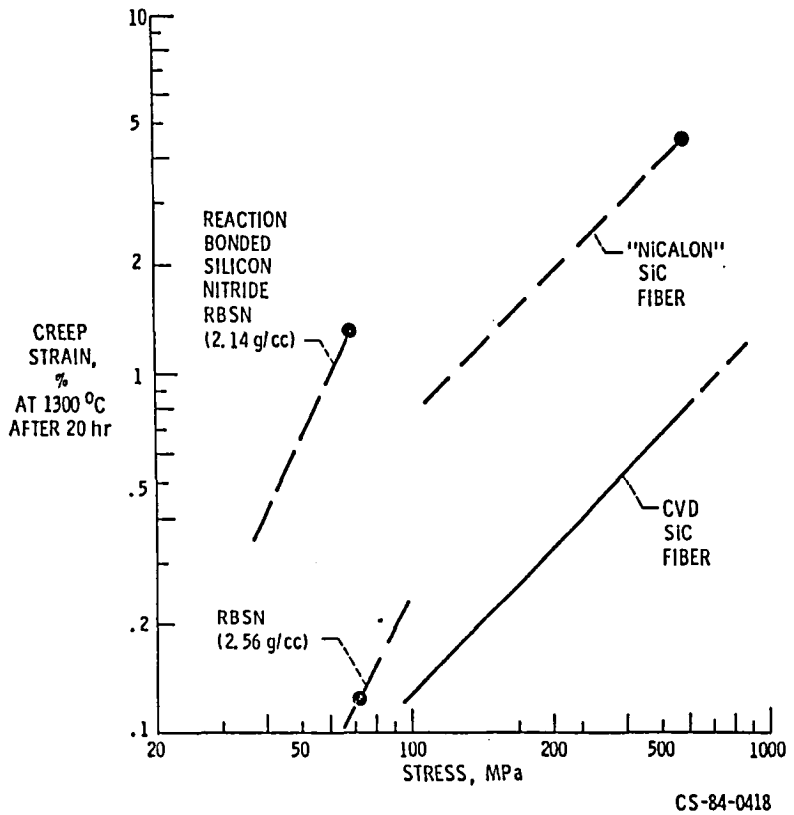
III. FIBER COATINGS

• OXYGEN EFFECTS ON COMMERCIAL COATINGS FOR CVD SiC FIBERS	- COATING DESIGN FOR OXIDATION RESISTANCE
• FIBER-MATRIX LOAD TRANSFER IN SiC/RBSN COMPOSITES	- COATING DESIGN FOR COMPOSITE TOUGHNESS AND STRENGTH

PROPERTY COMPARISON - COMMERCIAL SiC FIBERS

TYPE:	NiCALON (NIPPON CO.)	SCS (AVCO)
PRODUCTION METHOD:	POLYMER SPUN, CURED, PYROLYZED	CVD ONTO CARBON FILAMENT (1300 ^{o}C)
FORM:	MULTIFILAMENT YARN (500 PER TOW)	MONOFILAMENT
DIAMETER, μm:	10 TO 20	142
MODULUS, GPa:	180	390
STRENGTH, GPa:		
20 ^{o}C:	2.0	>3.5
1400 ^{o}C:	<1.0	>2.5

CVD SiC FIBERS PROVIDE CREEP RESISTANCE TO RBSN MATRICES



ADVANTAGES OF FIBER COATINGS FOR CERAMIC MATRIX COMPOSITES

PHYSICAL - CHEMICAL:

- CAN SERVE AS A DIFFUSION BARRIER INHIBITING INTERDIFFUSION AND REACTIONS WITH MATRIX AND AGGRESSIVE GASES, SUCH AS, OXYGEN
- MINIMIZE DEGRADATION OF FIBER STRENGTH AND FIBER-MATRIX INTERFACIAL BONDING

STRUCTURAL:

- REDUCE MECHANICAL DEGRADATION DURING HANDLING AND COMPOSITE PROCESSING
- REDUCE INTERNAL DEGRADATION BY TRAPPING EVOLVING GASES
- HEAL FIBER SURFACE FLAWS AND INCREASE FIBER STRENGTH
- PROVIDE WEAK FIBER-MATRIX BONDING FOR CRACK DEFLECTION AND TOUGH COMPOSITES

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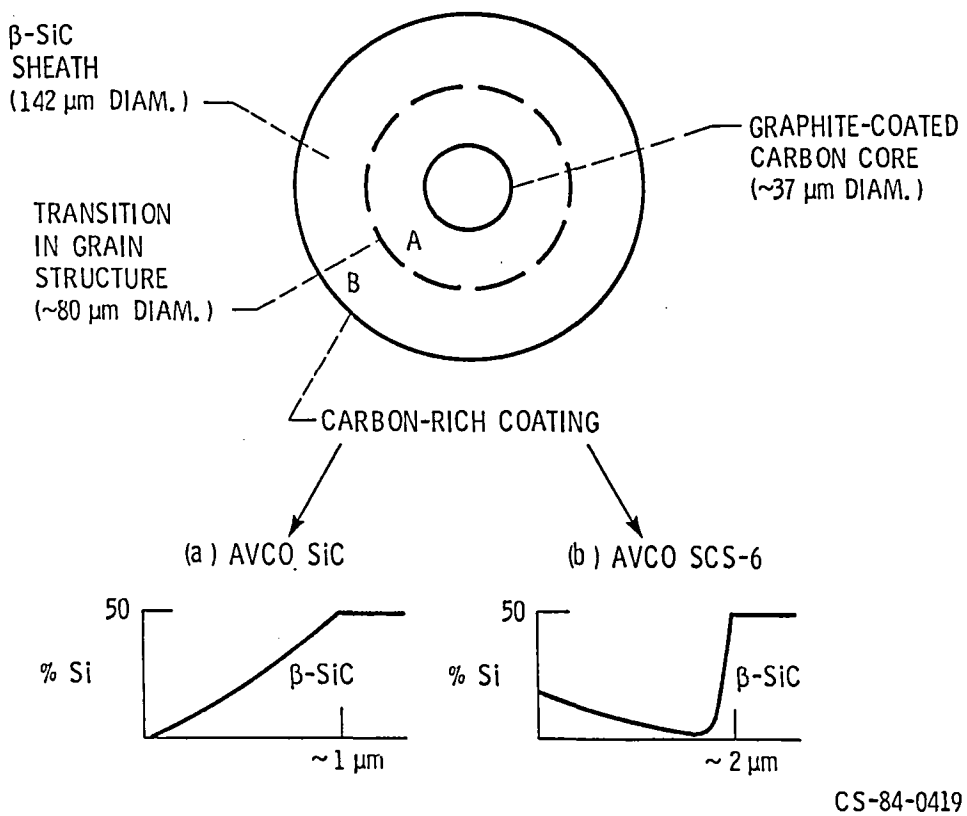
CVD SiC FIBER CROSS SECTION AND COATINGS



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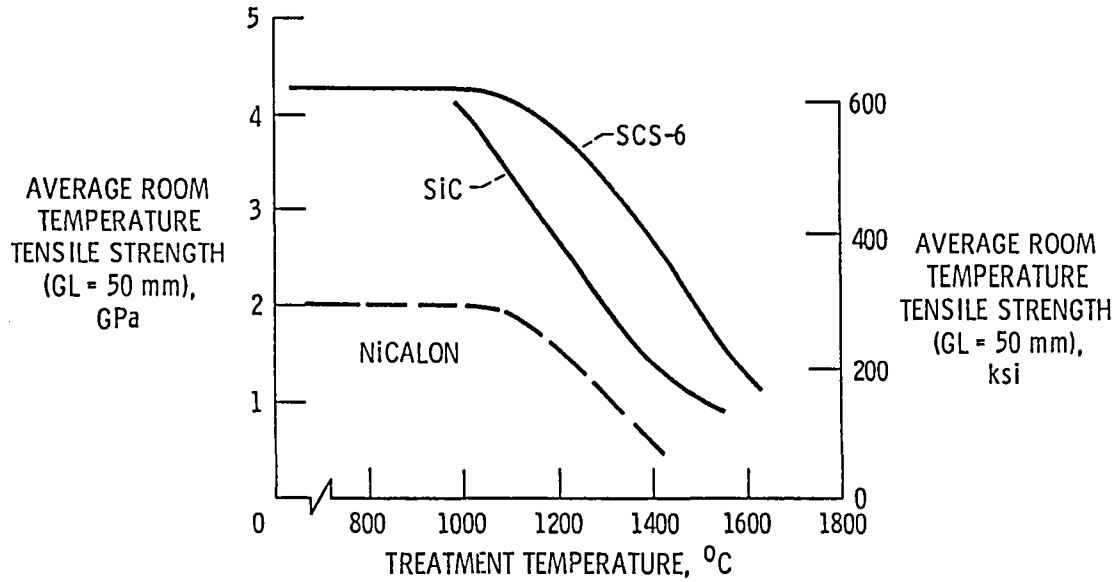
STRENGTH RETENTION OF SiC FIBERS

ARGON OR NITROGEN, 15 min (10^{-4} ATM OXYGEN)



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CERAMIC COMPOSITES - FUTURE DIRECTIONS

I. FRC FABRICATION
- SiC/RBSN OPTIMIZATION
- CVD-CVI PROCESSING
- COMBINED PROCESSING APPROACHES
- TOUGHENING ADDITIONS TO MATRIX
- MULTITYPE FIBERS AND FIBER WEAVES
- HYBRID MATRICES

II. HIGH PERFORMANCE CERAMIC FIBERS
- MULTIFILAMENT TOW OF SMALL DIAMETER CVD SiC FIBERS
- SINGLE CRYSTAL SiC AND OXIDE FIBERS
- NEW INNOVATIVE PROCESSING

III. FIBER COATINGS
- STABLE AND OPTIMIZED CVD SiC-C COATINGS
- OTHER CERAMIC COATINGS BY CVD, SOL-GEL, ETC

Polymer Precursors for SiC Ceramic Materials

by

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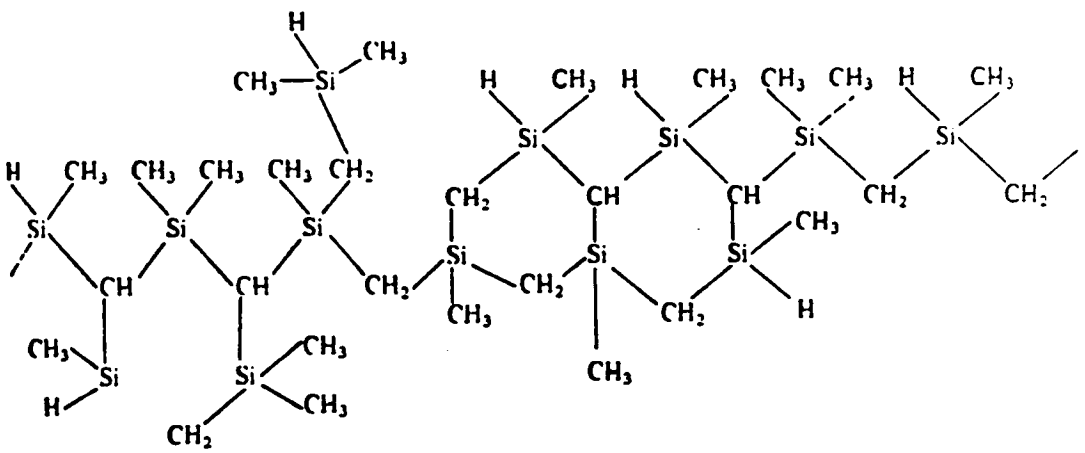
We have worked on precursor polymers to SiC, concentrating on polymers made from decamethyl cyclohexasilyene units. Our initial approach was to synthesize mixed diphenyl decamethyl cyclohexasilane, dephenylate and polymerize. This produced polymers which had yields of up to 50% SiC. [Theoretical yield is 75%.] Our present approach is to make polymer through the intermediate trans-1,4-diphenyl decamethyl cyclohexasilane. This should produce a crystalline polymer and high strength fibers. These will be thermally decomposed to SiC fibers. This requires new chemistry which we are studying now.

$$(CH_3)_2SiCl_2 \xrightarrow[\text{Xylene}]{\text{Na}} \left(\begin{array}{c} CH_3 \\ | \\ -Si- \\ | \\ CH_3 \end{array} \right)_x \xrightarrow[\Delta]{\text{sealed tube}}$$



$$PhMeSiCl_2 + 2Me_2SiCl_2 \xrightarrow[THF]{Na\text{-}K} Me_{12-x}Ph_xSi_6 + MCl$$

(x = 0-6) (M = Na,K)

TABLE 1. PERCENT YIELD OF VARIOUS ISOLATED DERIVATIVES

$Me_{12-x}Ph_xSi_6$ x	wt(%)	Yield mol(%)	mol(%)(theoretical)
0	8	11	8.8
1	24	27	26.3
2	32	32	32.9
3	36	30	21.9
4			8.2
5			1.6
6			0.1

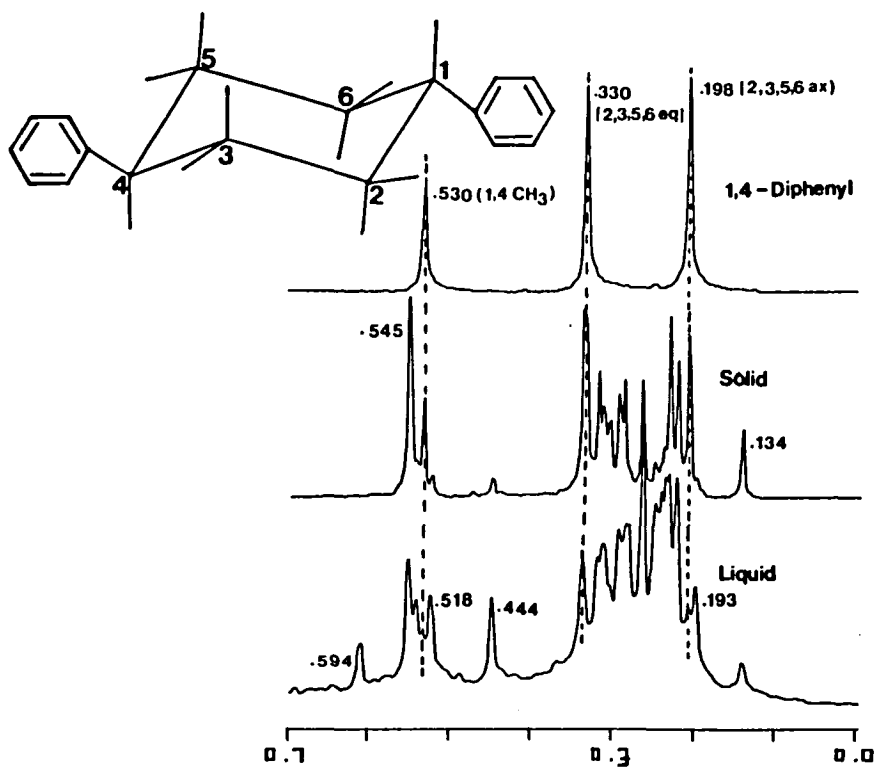


FIG 1. NMR OF DIPHENYLDECAMETHYLCYCLOHEXASILANE

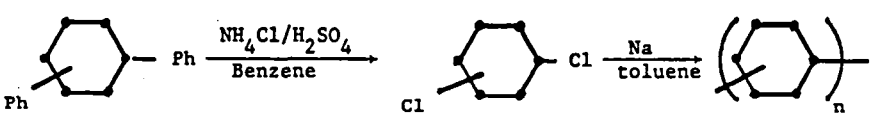
TABLE 2. ^{1}H-, ^{13}C-, AND ^{29}Si- NMR CHEMICAL SHIFTS FOR PURE 1,4-DIPHENYLDECAMETHYLCYCLOHEXASILANE

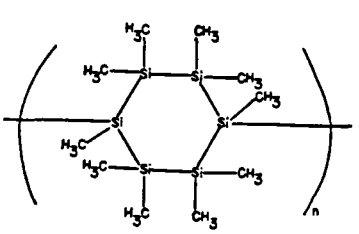
^{1}H(No. of Methyl Groups) (δ ppm)[a]	^{13}C(No. of Carbon) (δ ppm)[b]	^{29}Si(No. of Silicon) (δ ppm)[c]
0.530 (2)	-4.32 (4)	-41.08 (4)
0.330 (4)	-6.49 (2)	-41.40 (2)
0.198 (4)	-6.71 (4)	
	134.68 (o,4)	
	127.86 (p,2)	
	127.71 (m,4)	
	146.98 (i,2)	

a - CH_2Cl_2(δ 5.35) was used as an internal reference.

b - $CDCl_3$(δ 77.0) was used as an internal reference.

c - TMS(δ 0.0) was used as an internal reference.





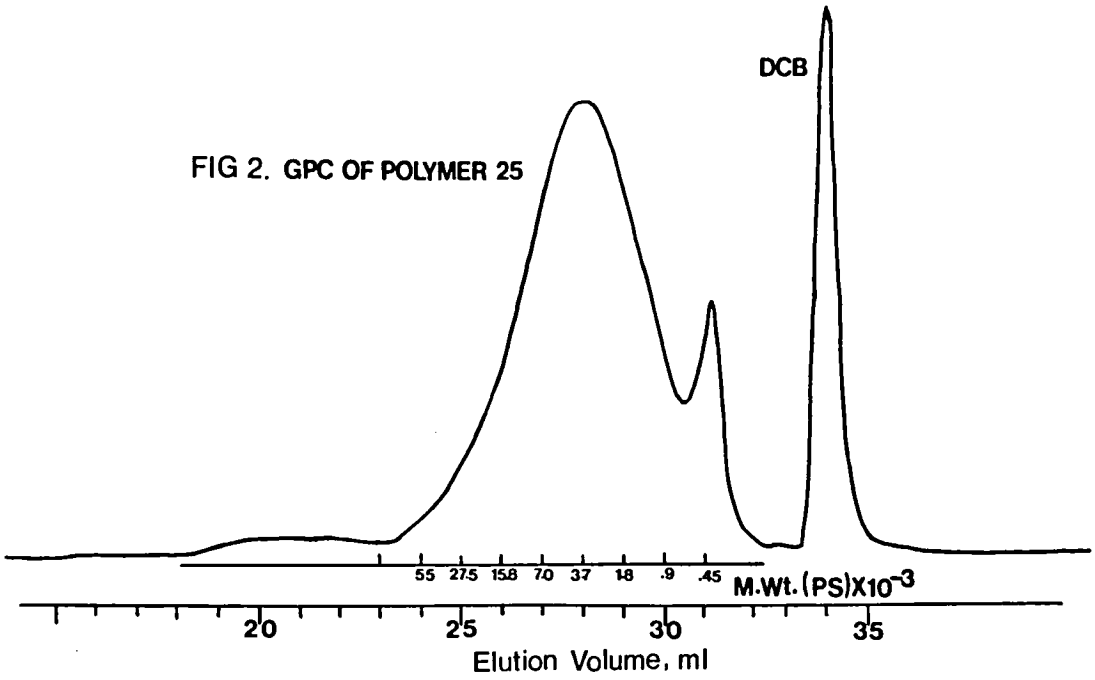


FIG 2. GPC OF POLYMER 25

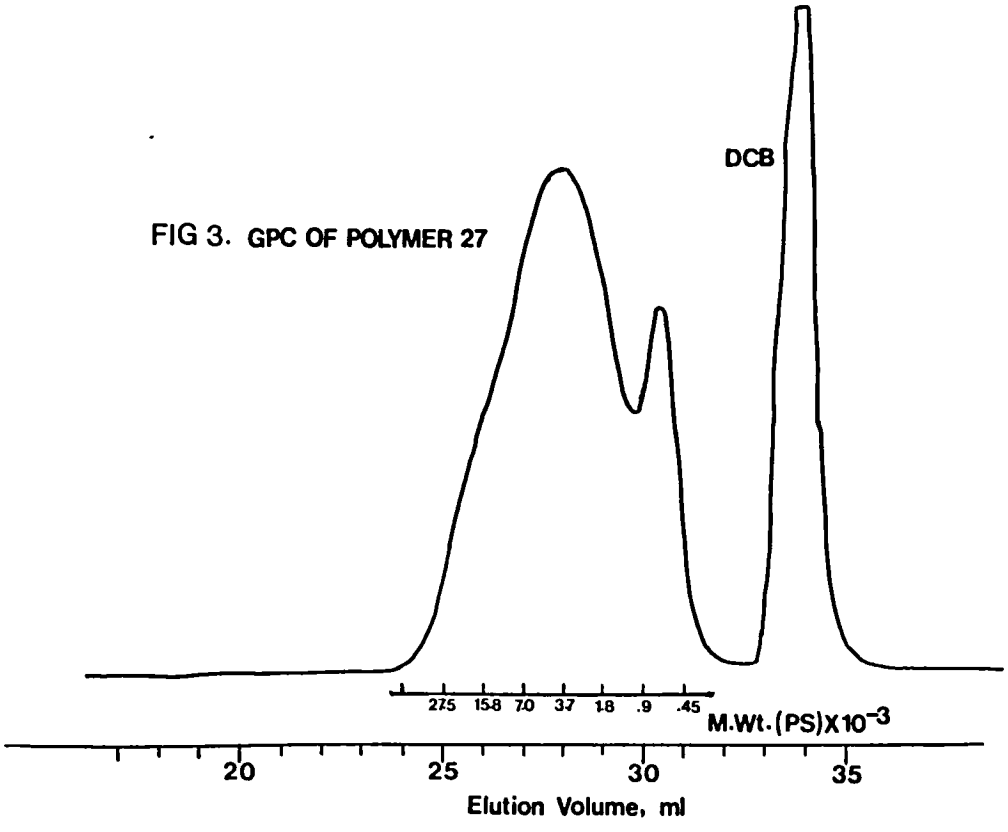


FIG 3. GPC OF POLYMER 27

TABLE 1 ELEMENTAL ANALYSIS OF POLYMER25 AND POLYMER27

Polymer	Analytical	% C	% H	% Si	% O
Polymer25	Calcd.:	37.74	9.43	52.83	0
	Found:	33.52	8.69	48.22	9.57 (by difference)
Repeat	Found:	34.40	8.51	-----	None or Trace
Polymer27	Calcd.:	37.74	9.43	52.83	0
	Found:	38.10	9.65	48.70	3.55 (by difference)
Repeat	Found:	40.14	9.23	-----	0.16

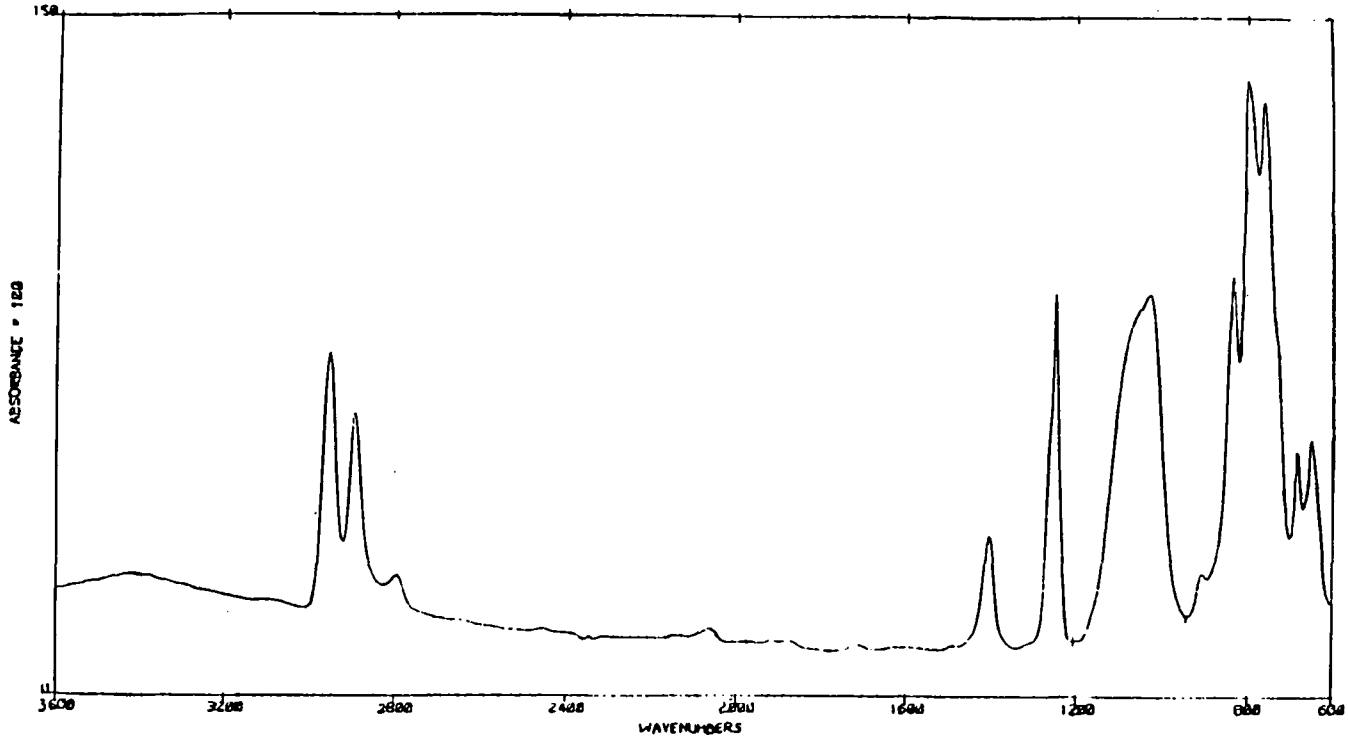


FIG 6. IR OF POLYMER25

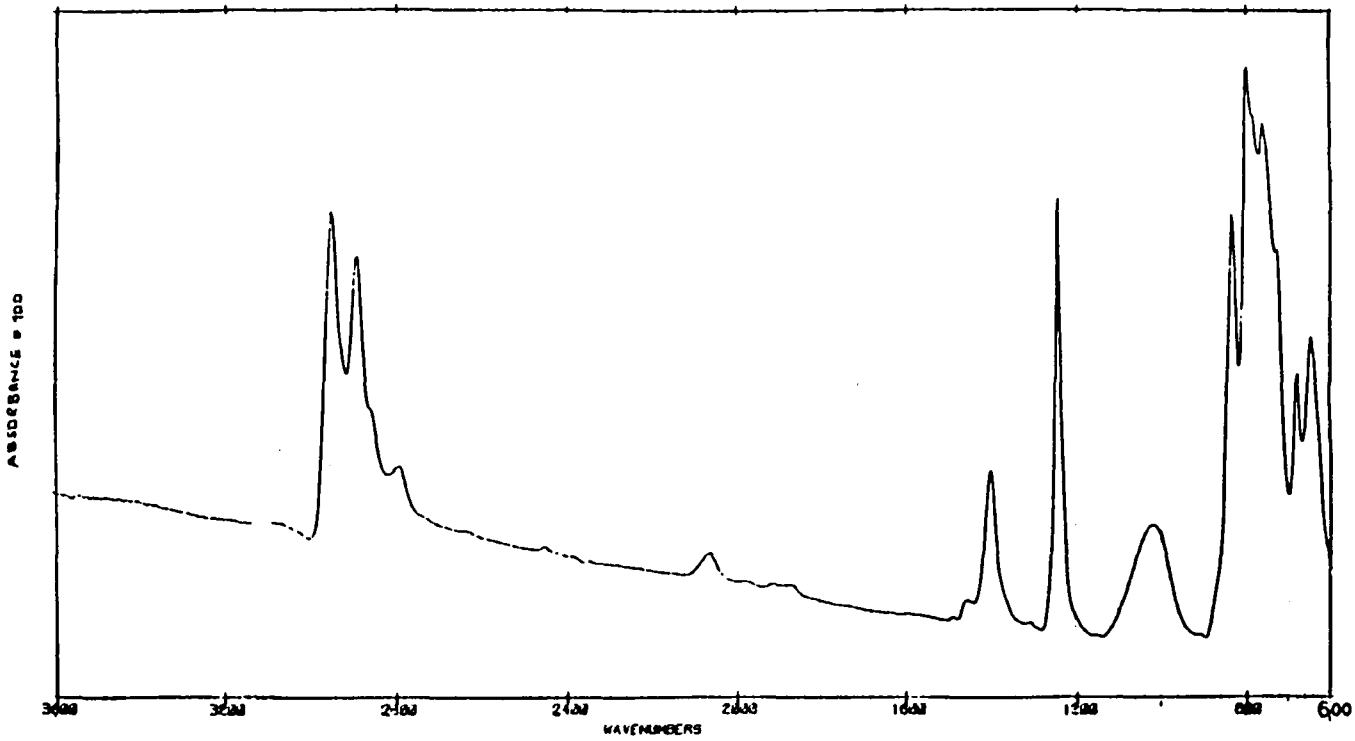


FIG 7. IR OF POLYMER27

TABLE 2 THERMOGRAVIMETRIC ANALYSIS OF POLYMER25 CURED AT VARIOUS TEMPERATURES

Temperature/Time	Char Yield %	Heating Rate
Polymer25	27.39	1.5°C/min
124° ± 4°C/4 hrs (a)	18.75	10° C/min
200° ± 1°C/5 min	20.85	10° C/min
250° ± 5°C/15 min	(a) 20.80	10° C/min
	(b) 48.27	10° C/min
200° ± 1°C/5 hrs	(c) 51.52	10° C/min
	17.74	10° C/min
	36.47	10° C/min
	25.71	15° C/min
	19.64	1.5°C/min

(a) Hexane soluble fraction (59.8% of total polymer).

(b) Gel (12.67% of the total polymer.

(c) A piece of polymer was used, rather than ground powder.

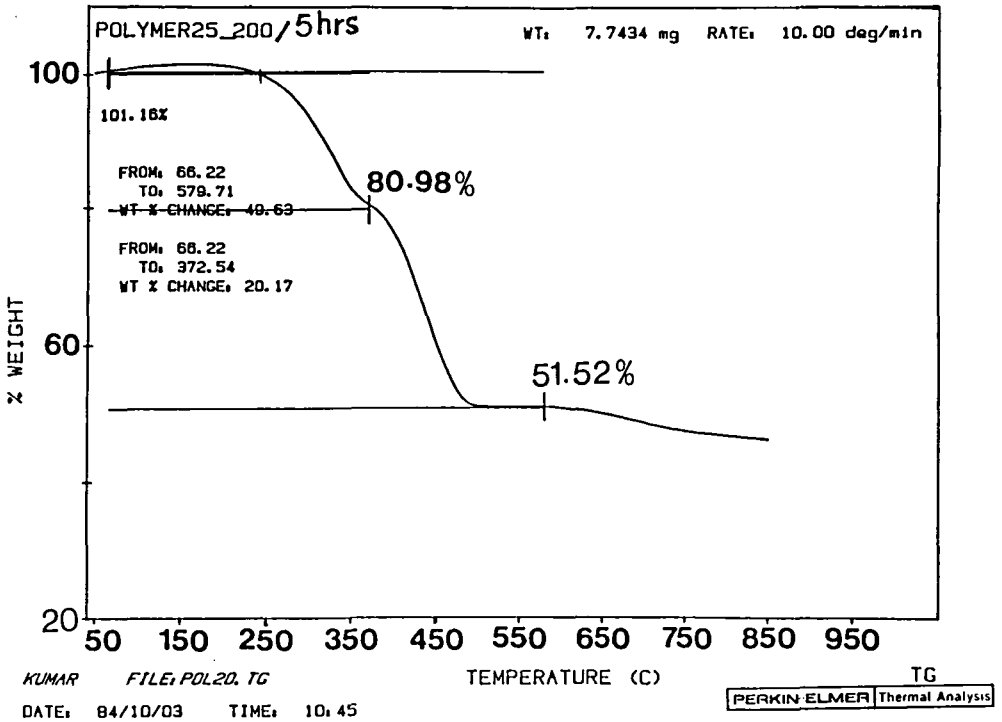
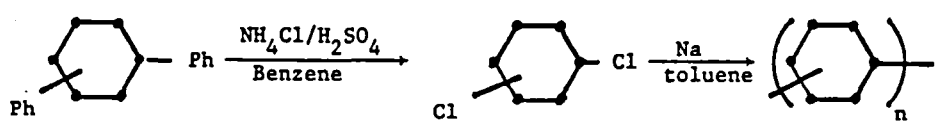


FIG 8. TGA

New Work

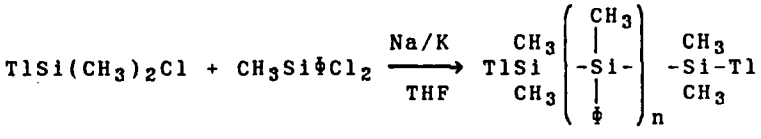
Trans-1,4-diphenyl decamethyl cyclohexasilane

mp = 169.5-170°C, yield = 0.2%



Poly(trans 1,4[1]-decamethyl cyclohexasilane)

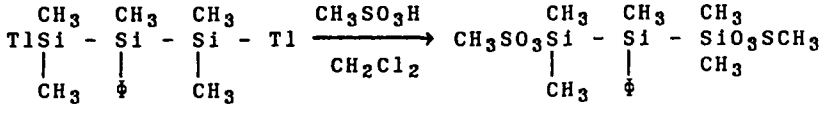
1. Crystallizable polymer.
2. Should be spinnable from solvent in nematic form.
3. Strong, stable fiber
4. Could retain strength to some degree during pyrolysis to SiC.
5. Higher yield and easier processing than present materials.



Tl = p-Tolyl n = 0 ⟶ ?

Theory - highest yield = 27% of n=1

Best yield so far = 20%, n=0,1,2,3,4 isolated



POLYMER PRECURSORS FOR CERAMIC COMPOSITES

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The fiber composite approach to reinforced ceramics provides the possibility of achieving ceramics with high fracture toughness relative to monolithics. Fabrication of ceramic composites, however, demands low processing temperatures to avoid fiber degradation. Formation of complex shapes further requires small diameter fibers as well as techniques for infiltrating the matrix between fibers.

Polymers offer low temperature processability, control of rheology not available with ceramic powders, and could serve as precursors to fibers of matrix. In recent years, a number of polysilanes and polysilezanes have been investigated as potential precursors. A review of candidate polymers will be presented, including recent studies of silsesquioxanes underway at LeRc.

NEEDS

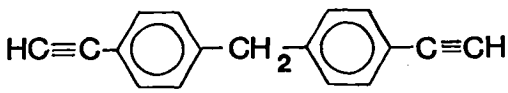
- SMALL DIAMETER CERAMIC FIBER
- HIGH TEMPERATURE, ENVIRONMENTALLY RESISTANT MATRIX

PROBLEMS

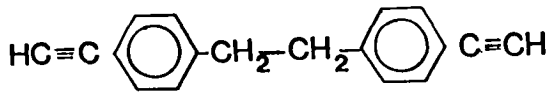
- LOW CHAR YIELD
- HIGH SHRINKAGES - VOIDS
- NEED FOR REPEATED IMPREGNATION
- DEVIATION FROM STOICHIOMETRY - CHEMICAL INSTABILITY AT HIGH TEMPERATURES

$$\text{POLYMER} + \begin{matrix}\text{CERAMIC}\\ \text{PARTICULATE}\end{matrix} + \begin{matrix}\text{CONTINUOUS}\\ \text{FILAMENT}\end{matrix} \xrightarrow[\text{pyrolyze}]{\text{hot press}} \begin{matrix}\text{HIGH TEMPERATURE}\\ \text{COMPOSITE}\end{matrix}$$

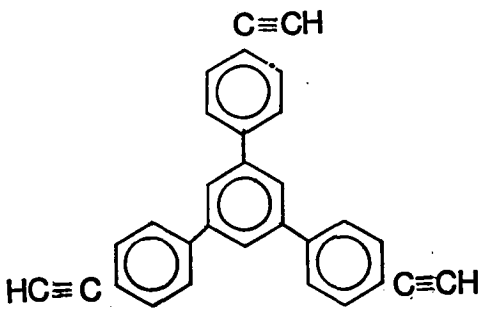
MONOMERS



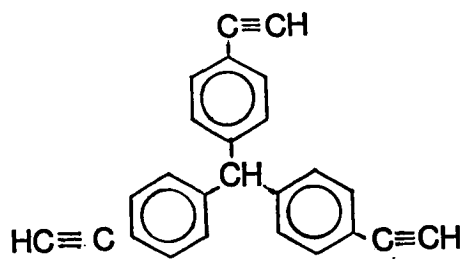
DEDPM
diethynyldiphenylmethane



DEDPE
diethynyldiphenylethane

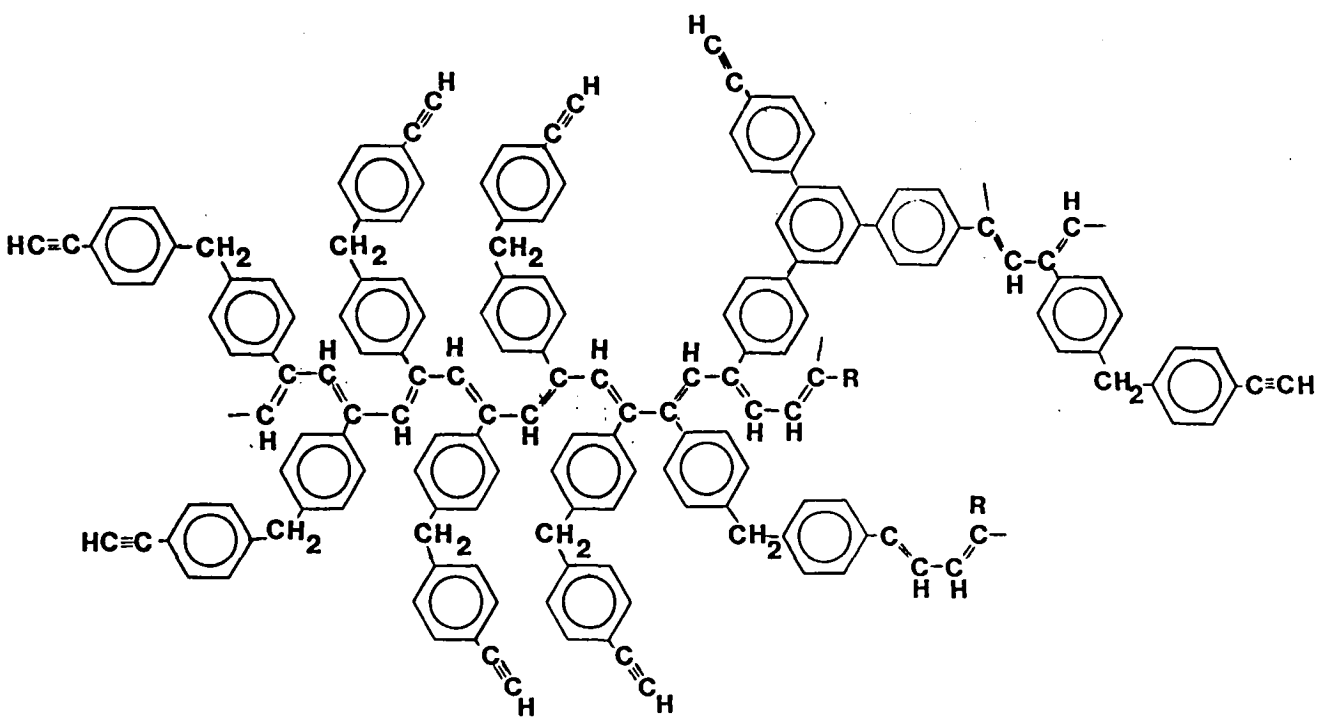


TETPB
triethynyltriphenylbenzene

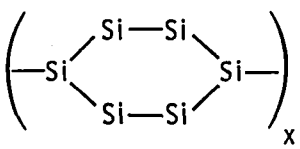


TETPM
triethynyltriphenylmethane

CROSSLINKED HOMOPOLYMER OR COPOLYMER



Si CONTAINING POLYMERS

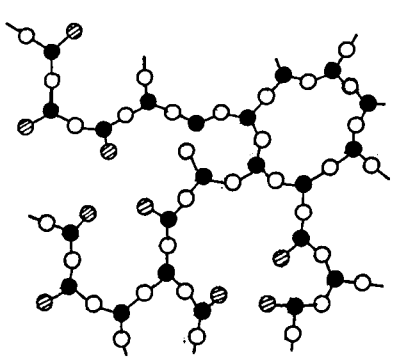
$(CH_3)_xSi_y$	METHYLPOLYSILANE
$((CH_3)_2SiCH_2SiHCH_3)_x$	POLYCARBOSILANE
$(C_6H_6CH_3Si)_x((CH_3)_2Si)_y$	POLYSILASTYRENE
$(CH_3Si)_x(CH_2CHSiCH_3)_y$	VINYLSILANE
$(CH_3HSiN)_x$	POLYMETHYLSILAZANE
$(CH_3Si)_x(NCH_3)_y(NHCH_3)_z$	POLYCARBOSILAZANE
	POLY (CYCLOHEXAMETHYLSILANE)

SILSESQUIOXANES

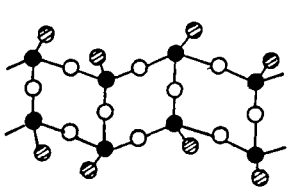
$RSiO_{1.5}$

R = methyl, propyl, vinyl, phenyl

T Resin



Ladder Polymer



SiC FIBER ANALYSIS

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NASA Lewis Research Center
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Polymer derived Nicalon SiC fibers are known to be thermally unstable at temperatures beyond 1200°C. In an effort to further understand the mechanisms of fiber degradation, Nicalon fibers were heat treated at temperatures up to 2200°C and argon gas pressures varying from 0 to 1360 atm. The effects of gas pressure on the thermal stability of the fibers were determined through property comparisons between the pressure-treated fibers and vacuum-treated fibers. Investigation of the thermal stability included studies of the fiber microstructure and mechanical and physical properties before and after treatments.

Nicalon Fiber Thermal Stability

Problem:

- Polymer derived Nicalon SiC fibers degrade significantly in tensile strength above 1200 C in inert environments

Probable Mechanisms:

- Creation of increased internal porosity and flaw growth caused by reactions between SiC, SiO_2, C, and Si_3N_4 in the as-produced fiber

- Grain growth of microcrystalline SiC

Objectives

- To determine the effects of heat treatment in high pressure argon on the tensile strength and physical properties of commercially available Nicalon SiC fibers

- To determine whether Hot Isostatic Pressing can offer a viable approach to improving the thermal stability of Nicalon fibers

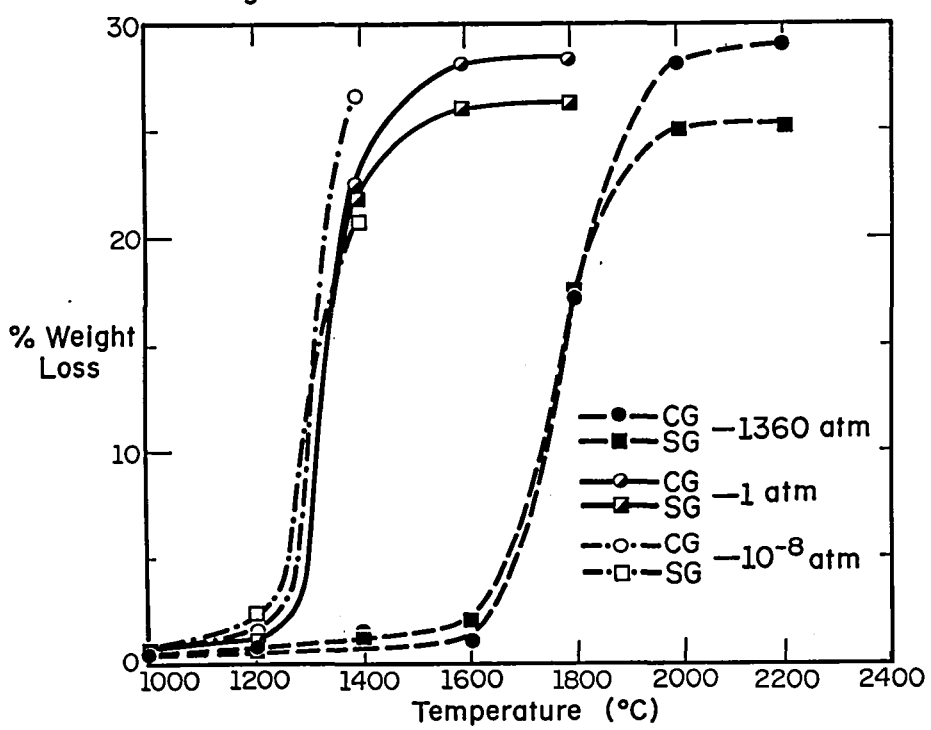
Experimental Parameters

		Si	C	O	N	
Nicalon Fibers:	Ceramic Grade	~40	50	8	2	at%
	Standard Grade	~37	46	15	2	at%

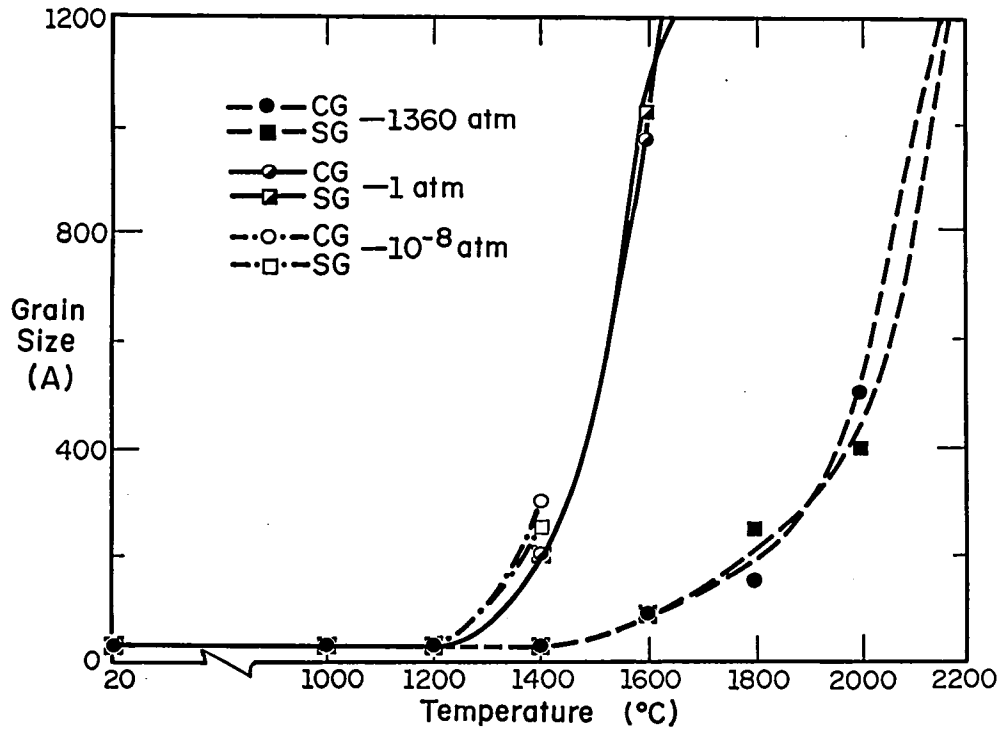
Treatment Conditions: Pressure: 10 , 1, 1360 atm Argon
Temperature: 1000 - 2200 C
Time: 1 hour

Properties: Weight Loss
Tensile Strength
Grain Size
Microstructure
Crystalline Phases

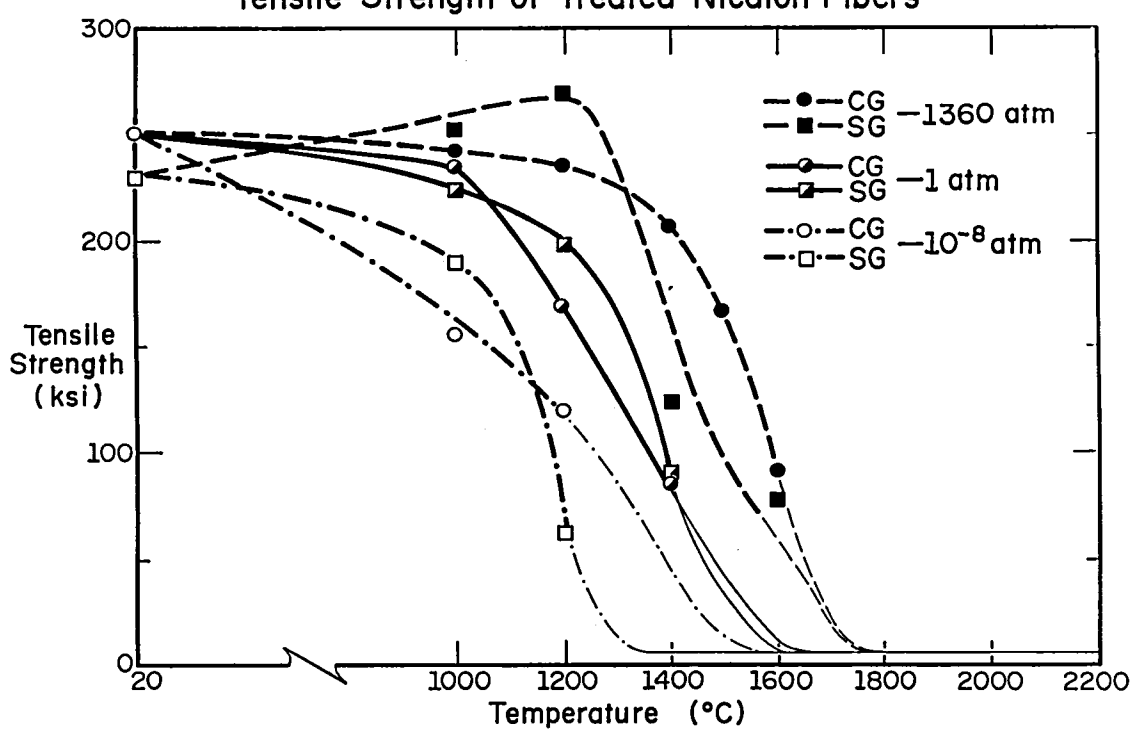
Pressure and Temperature Effects on the Weight Loss of Treated Nicalon Fibers



Pressure and Temperature Effects on the
Grain Growth of Treated Nicalon Fibers

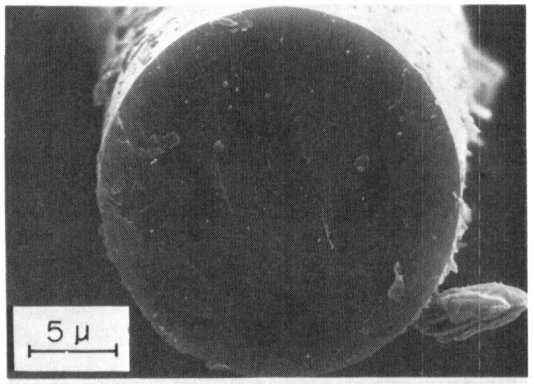


Pressure and Temperature Effects on the
Tensile Strength of Treated Nicalon Fibers

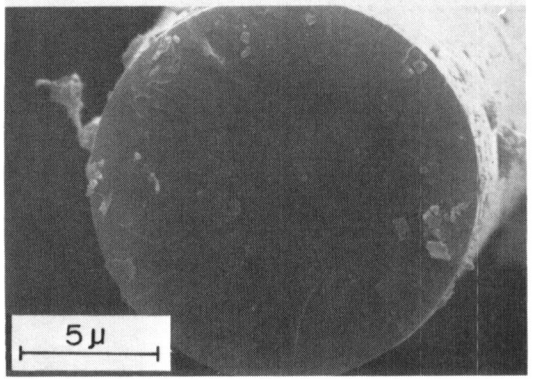


Fracture Surfaces of As-Received Nicalon Fibers

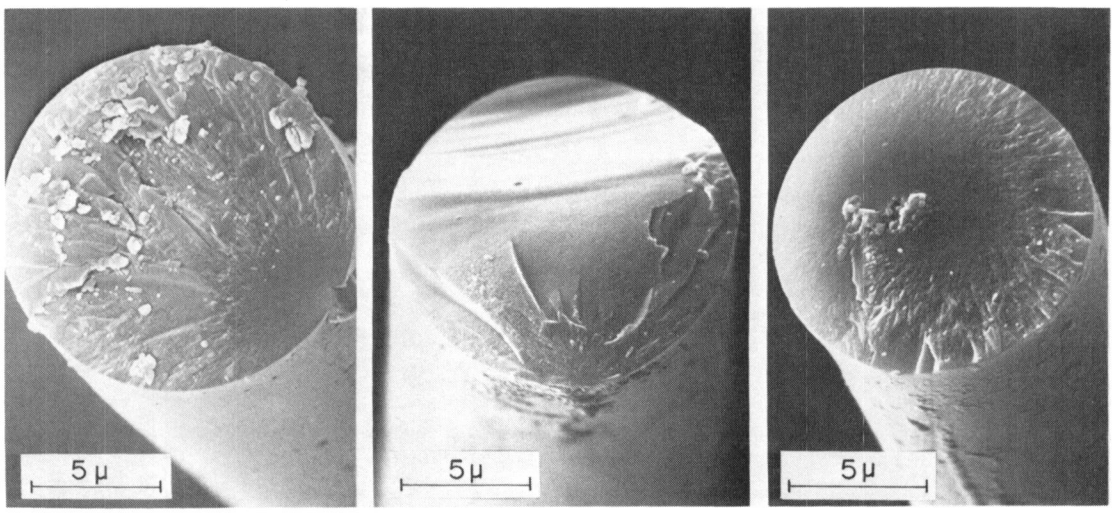
Standard Grade 250 ksi



Ceramic Grade 231 ksi



Ceramic Grade Nicalon Heated to 1000 °C

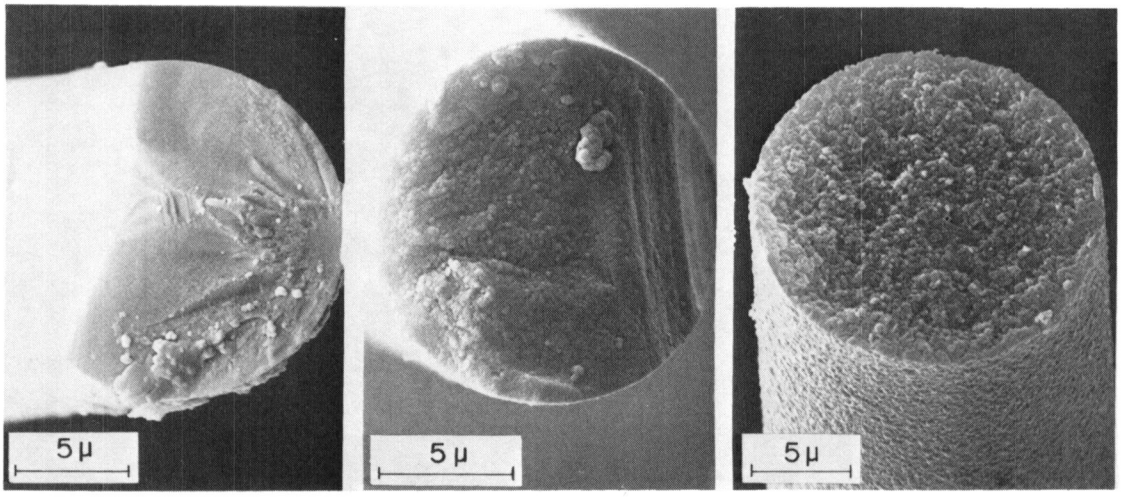


1360 atm
0.6 % wt loss
240 ksi

1 atm
0.8 % wt loss
235 ksi

10^{-8} atm
0.8 % wt loss
154 ksi

Ceramic Grade Nicalon Heated to 1400 °C



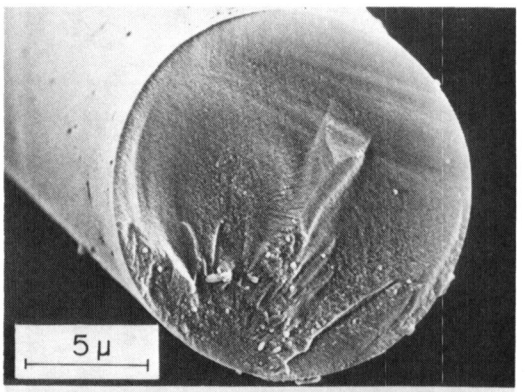
1360 atm
1.0 % wt loss
208 ksi

1 atm
22 % wt loss
85 ksi

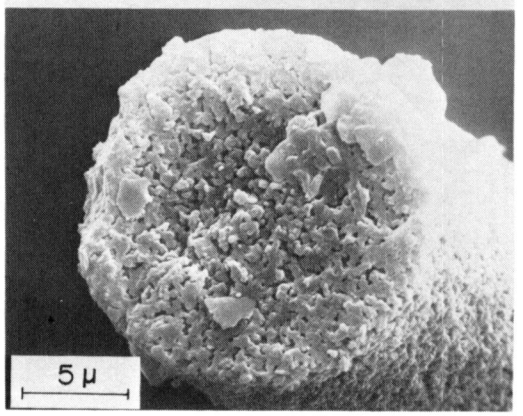
10^{-8} atm
27 % wt loss
— ksi

Ceramic Grade Nicalon Fibers Heated to 1600 °C

1360 atm
0.8 % wt loss
90 ksi

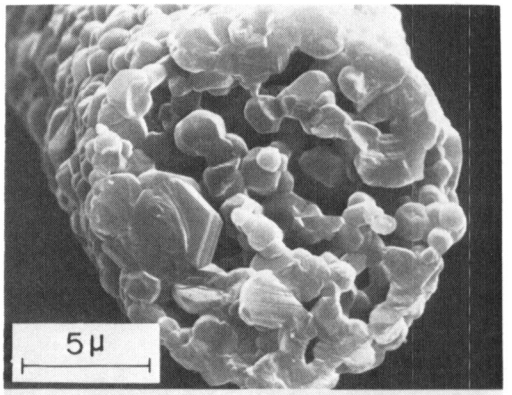


1 atm
28 % wt loss
— ksi

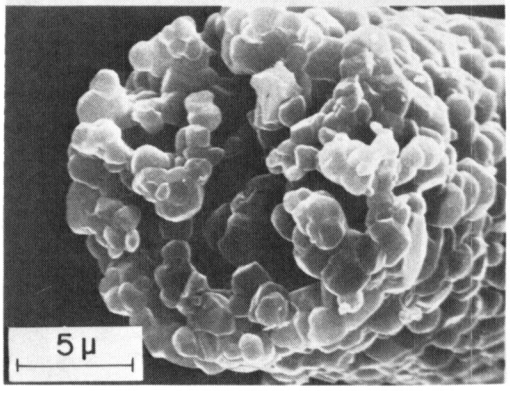


Nicalon Fibers Heated to 2200°C

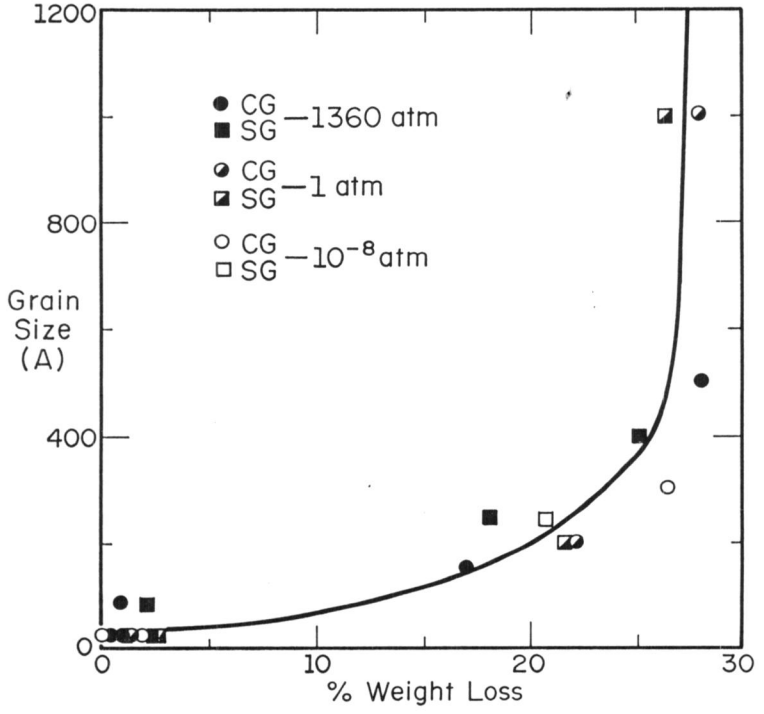
Standard
Grade
1360 atm
25 % wt loss
— ksi



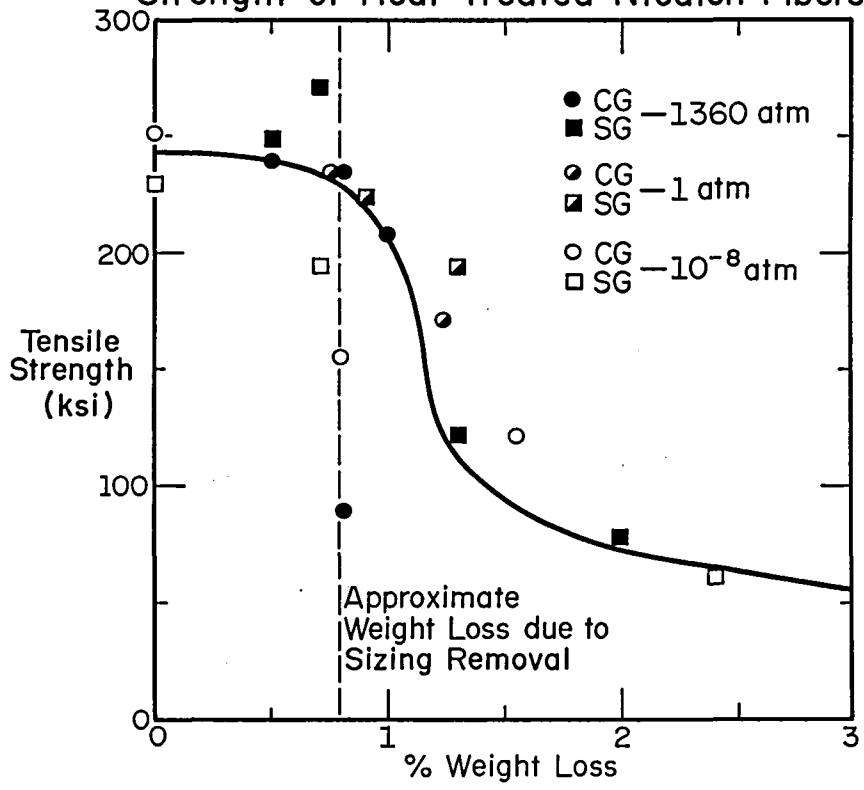
Ceramic
Grade
1360 atm
28 % wt loss
— ksi



Correlation Between Weight Loss and
Grain Growth of Heat Treated Nicalon Fibers



Effect of Weight Loss on the Tensile Strength of Heat Treated Nicalon Fibers



Results of Additional Heat Treatment Tests on High Pressure Treated Nicalon Fibers

Heat Treatment Conditions	% Weight Loss CG / SG	Tensile Strength (ksi) CG / SG
1200 C – 1 hr 1360 atm Ar	0.8 / 0.7	236 / 271
1200 C – 1 hr 1360 atm Ar 1400 C – 1 hr 1 atm Ar	28 / 24	-- --
1600 C – 1 hr 1360 atm Ar	0.8 / 2.0	90 / 78
1600 C – 1hr 1360 atm Ar 1400 C – 1 hr 1 atm Ar	23 / 26	-- --

Pressure Effects on Nicalon Thermal Stability

Summary:

- High pressure treatments in Argon suppress fiber weight loss to temperatures above 1500 C
- Strength degradation and grain growth can be correlated with weight loss and thus are also inhibited by high pressure treatments
- Strength degradation occurs rapidly within the first 1% weight loss (beyond the sizing removal) whereas grain growth does not proceed as rapidly until ~20% weight is reached
- Fibers retreated at 1400 C in 1 atm Ar after high pressure treatment show no improvement in strength over as received fibers treated at 1400 C

Pressure Effects on Nicalon Thermal Stability

Conclusions:

- Increased external pressure creates a diffusion barrier which inhibits CO gas evolution from internal SiO_2 – Carbon reactions thus suppressing fiber weight loss
- Suppression of CO gas evolution may also delay exaggerated grain growth due to the tendency of excess carbon in SiC to act as a grain growth inhibitor
- Initial and major strength degradation mechanism is most likely due to the rapid growth of pre-existing flaws near the surface
- In general, high pressure treatment of commercial Nicalon fibers offers no improvement in thermal stability unless pressure can be maintained throughout composite fabrication and fiber use
- Because of initial porosity and/or creep resistance in the as-produced Nicalon fibers Hot Isostatic Pressing does not appear to be an effective post-fabrication method for improving fiber thermal stability

Fiber Development – Future Directions

Based on potential SiC Properties:

- High modulus (>400 GPa)
- High strength (>4 GPa)
- Creep resistance
- Environmental resistance
- Low density
- High thermal conductivity
- Property retention to above 1400 C

Efforts will continue to develop processing approaches for producing

- Continuous
- Small diameter
- High performance
- Multifilament tows of SiC fibers

Current results indicate CVD Processing as the optimum approach for the base fibers and for required fiber coatings

SiC FIBER REINFORCED REACTION-BONDED Si_3N_4 COMPOSITES

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NASA Lewis Research Center
Cleveland, Ohio 44135

A technique for fabricating strong and tough SiC fiber reinforced reaction bonded Si_3N_4 matrix composites (SiC/RBSN) has been developed. Using this technique, composites containing ~ 23, 30, and 40 volume fractions of aligned 140 μm diameter, chemically vapor deposited SiC fibers have been fabricated. The room temperature physical and mechanical properties have been evaluated. The results for composite tensile strength, bend strength, and fracture strain indicate that the composite displays excellent properties when compared with the unreinforced matrix of comparable porosity. The composite stress at which the matrix first cracks and the ultimate composite fracture strength increase with increasing volume fraction of fibers, and the composite fails gracefully.

Measurements of room temperature tensile strength of SiC/RBSN composites after 100 hr exposure in flowing air at 1200°C and at 1400°C, and measurements of bend strength at temperatures up to 1300°C did not show any appreciable strength loss from the strength values of as-fabricated composites. The mechanical property data of this ceramic composite are compared with similar data for unreinforced commercially-available Si_3N_4 materials and for SEP SiC/SiC composites.

SiC FIBER REINFORCED REACTION - BONDED Si_3N_4

by

R. T. BHATT

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CLEVELAND, OHIO 44135

OBJECTIVE:

- TO FABRICATE AND EVALUATE PROPERTIES OF FIBER REINFORCED Si_3N_4 MATRIX COMPOSITES FOR ADVANCED HEAT ENGINE APPLICATIONS

RATIONALE:

- Si_3N_4 IS A LIGHT, OXIDATION RESISTANT, THERMAL SHOCK RESISTANT, NONSTRATEGIC MATERIAL BUT LACKS DUCTILITY (TOUGHNESS) AND STRENGTH REPRODUCIBILITY

APPROACH:

- REINFORCEMENT OF Si_3N_4 BY HIGH STRENGTH, HIGH MODULUS CERAMIC FIBER SHOULD
  - IMPROVE TOUGHNESS BY CRACK DEFLECTION AT THE INTERFACE
  - INCREASE FIRST MATRIX FAILURE STRESS DUE TO INCREASE IN STIFFNESS OF MATERIAL

PROPERTIES:

- FIRST MATRIX CRACK STRESS
- ULTIMATE STRENGTH
- INTERFACIAL SHEAR STRENGTH
- THERMAL SHOCK RESISTANCE
- THERMAL STABILITY

TESTS:

- TENSILE STRENGTH - (ROOM TEMPERATURE)
- FLEXURE STRENGTH - (ROOM TEMPERATURE TO 1400 ^{o}C)

MATERIALS FOR Si_3N_4 COMPOSITE

FIBERS

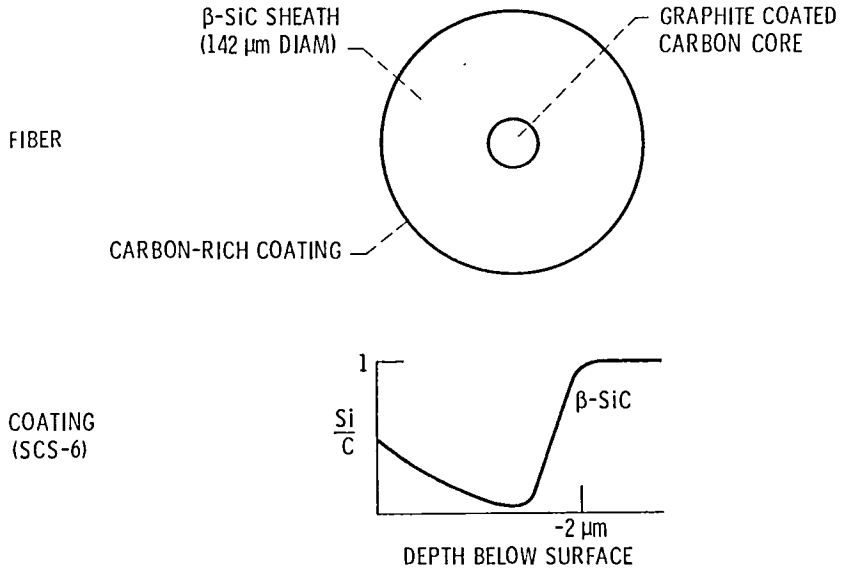
- AVCO CVD SILICON CARBIDE FIBERS
- HIGH MODULUS - 390 GPa ($57x10^6$ psi)
- HIGH STRENGTH - 3.5 GPa (500 ksi)
- HIGH PURITY
- CREEP RESISTANT
- COMPATABLE WITH Si_3N_4

MATRIX

- REACTION-BONDED SILICON NITRIDE
- LOW MODULUS - 100-200 GPa ($15\text{-}30x10^6$ psi)
- LOW TEMPERATURE FABRICATION
- NET SHAPE PROCESSING

CD-85-16631

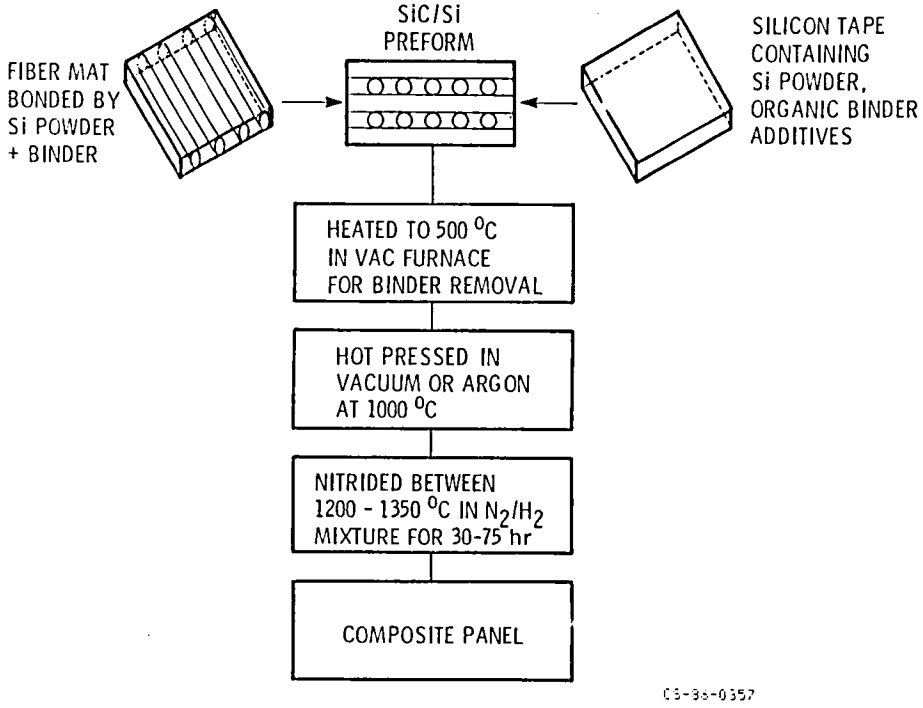
AVCO SiC FIBER COMPOSITION



CD-85-16632

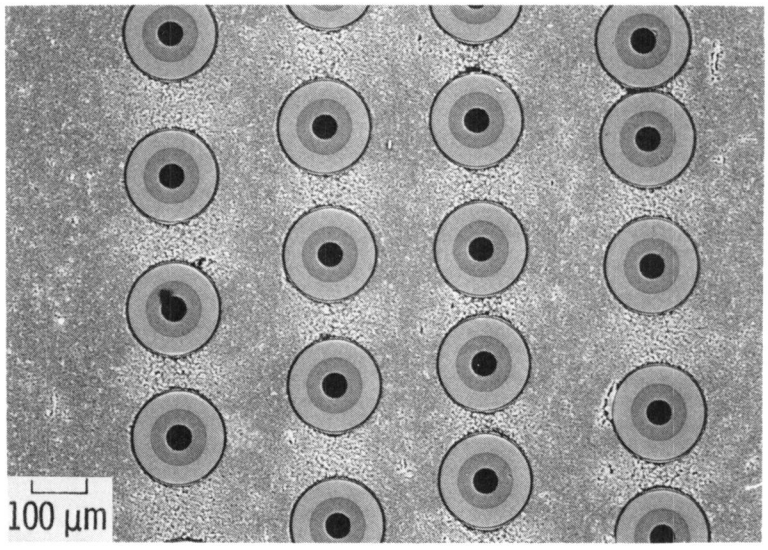
CS-85-2221

SiC/RBSN COMPOSITE FABRICATION



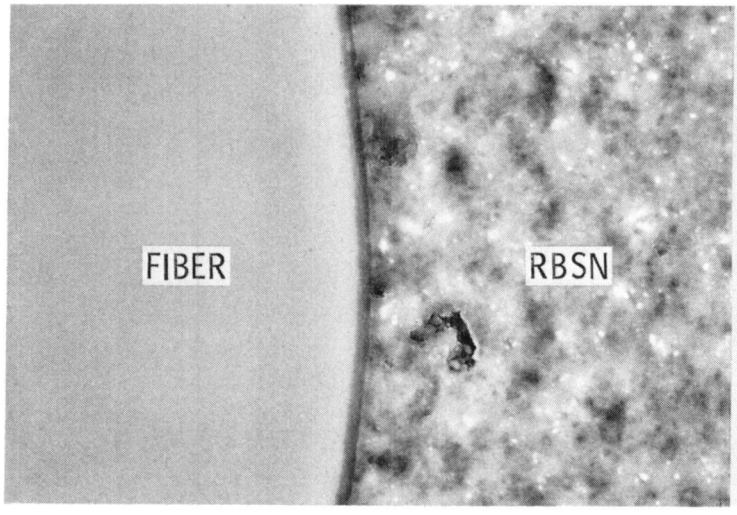
CS-86-0357

CROSS SECTION OF 39 VOL% SiC/RBSN COMPOSITE

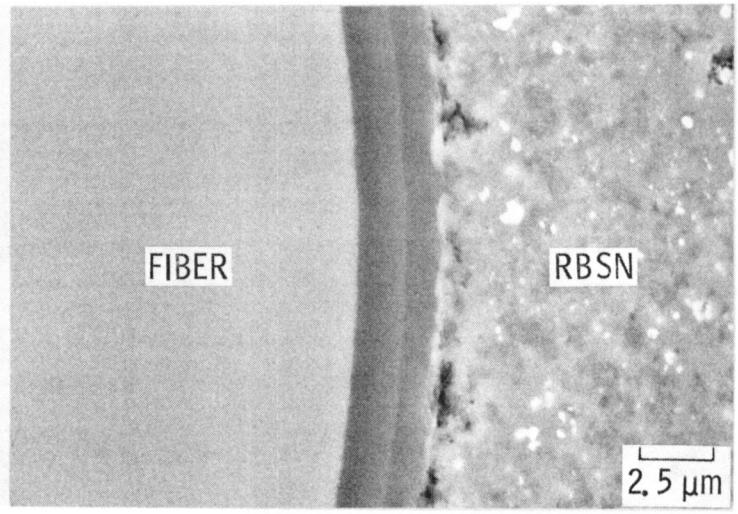


CS-86-0199

INTERFACIAL REGION IN SiC/RBSN COMPOSITE



SCS-0 FIBER



SCS-6 (DOUBLE COATED) FIBER

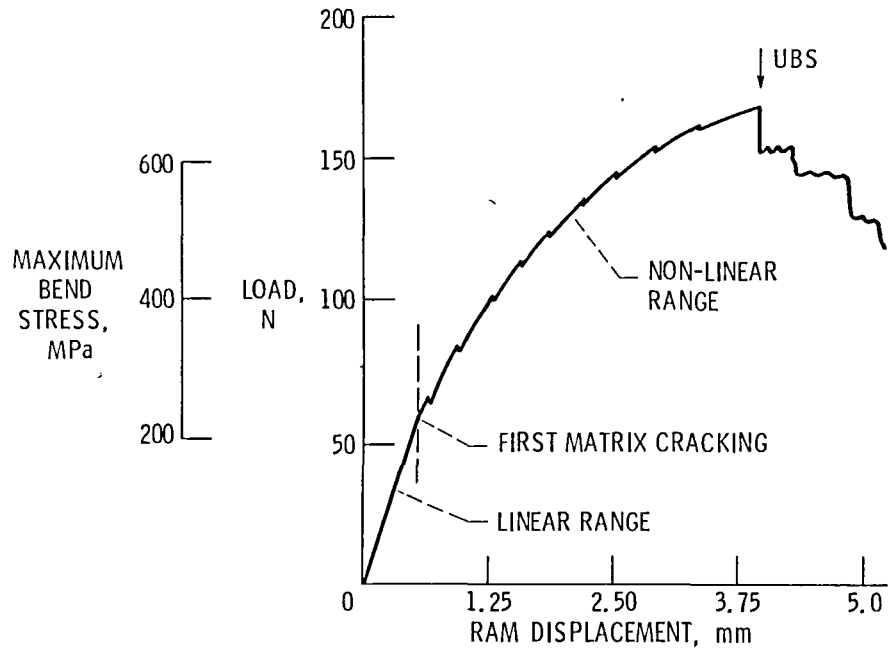
CS-86-0200

DENSITY AND POROSITY DATA FOR SiC/RBSN COMPOSITES

VOLUME FRACTION OF FIBERS	BEFORE NITRIDATION		AFTER NITRIDATION	
	DENSITY gm/cc	MATRIX POROSITY, %	DENSITY gm/cc	MATRIX POROSITY, %
0	1.56	35	1.98	37
23 ± 3	1.70	54	2.19	39
40 ± 2	1.90	51	2.36	40

CD-85-16629

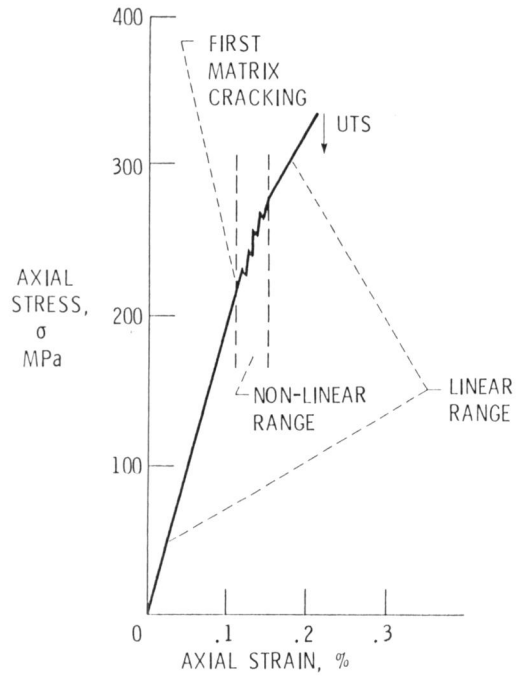
THE LOAD-DISPLACEMENT BEHAVIOR FOR 20 vol % SiC/RBSN COMPOSITE IN 3-POINT BENDING



CD-85-16628

CS-85-2217

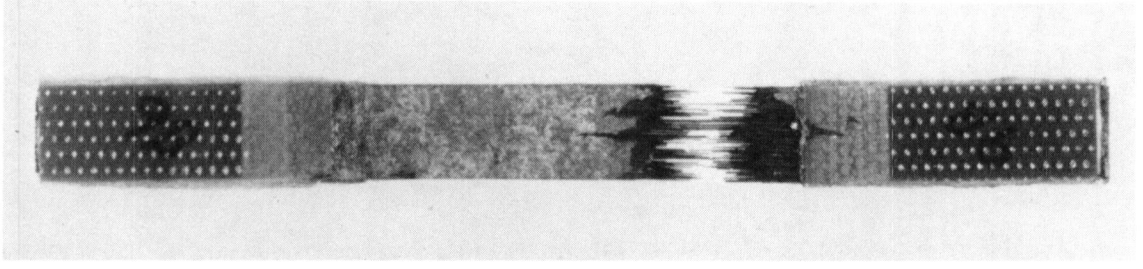
THE AXIAL STRESS-STRAIN BEHAVIOR FOR 20 vol %
SiC/RBSN COMPOSITE



CD 85-16630

CS-85-2220

FRACTURED TENSILE SPECIMEN OF SiC/RBSN COMPOSITE



ROOM TEMPERATURE STRENGTHS OF SiC/RBSN COMPOSITE

TEST	AXIAL STRENGTH, MPa		
	0% FIBER	23 ± 3% FIBER	40 ± 2% FIBER
4 POINT BEND ($\frac{L}{h}$ = 15)[a]	107 ± 26	539 ± 48	616 ± 36
4 POINT BEND ($\frac{L}{h}$ = 45)	-------	675 ± 42	868 ± 32
3 POINT BEND ($\frac{L}{h}$ = 35)	-------	717 ± 80	958 ± 45
TENSILE[b]	-------	352 ± 73	536 ± 20

[a]TEST SPECIMEN HEIGHT ≈ 1.25 mm

[b]TEST GAUGE LENGTH 50 mm

CD-85-16641

CS-85-2218

SiC/RBSN FRACTURE PARAMETERS

FIBER FRACTION, %	MATRIX CRACK SPACING, mm	INTERFACIAL SHEAR STRESS[a], MPa	COMPOSITE STRESS AT WHICH MATRIX FIRST CRACKED, MPa	MATRIX FRACTURE STRAIN[b]
23 ± 3	2.0 ± 0.3	10.91	237 ± 25	0.0015
40 ± 2	0.9 ± 0.2	10.23	293 ± 15	0.0014

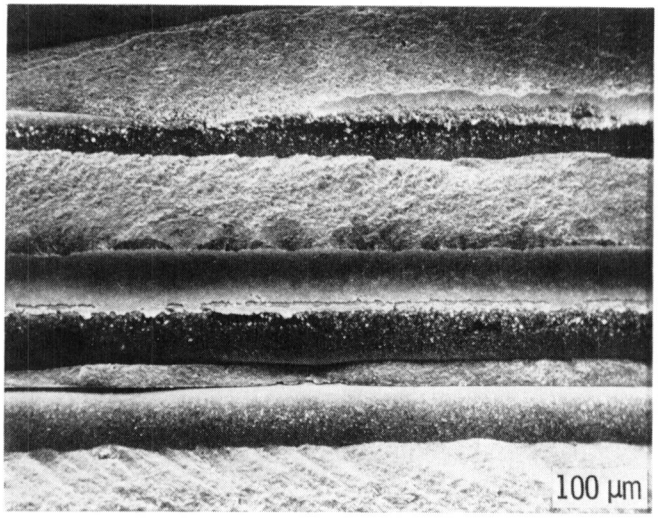
[a]CALCULATED FROM ACK THEORY

[b]CALCULATED FROM ESTIMATED COMPOSITE MODULUS

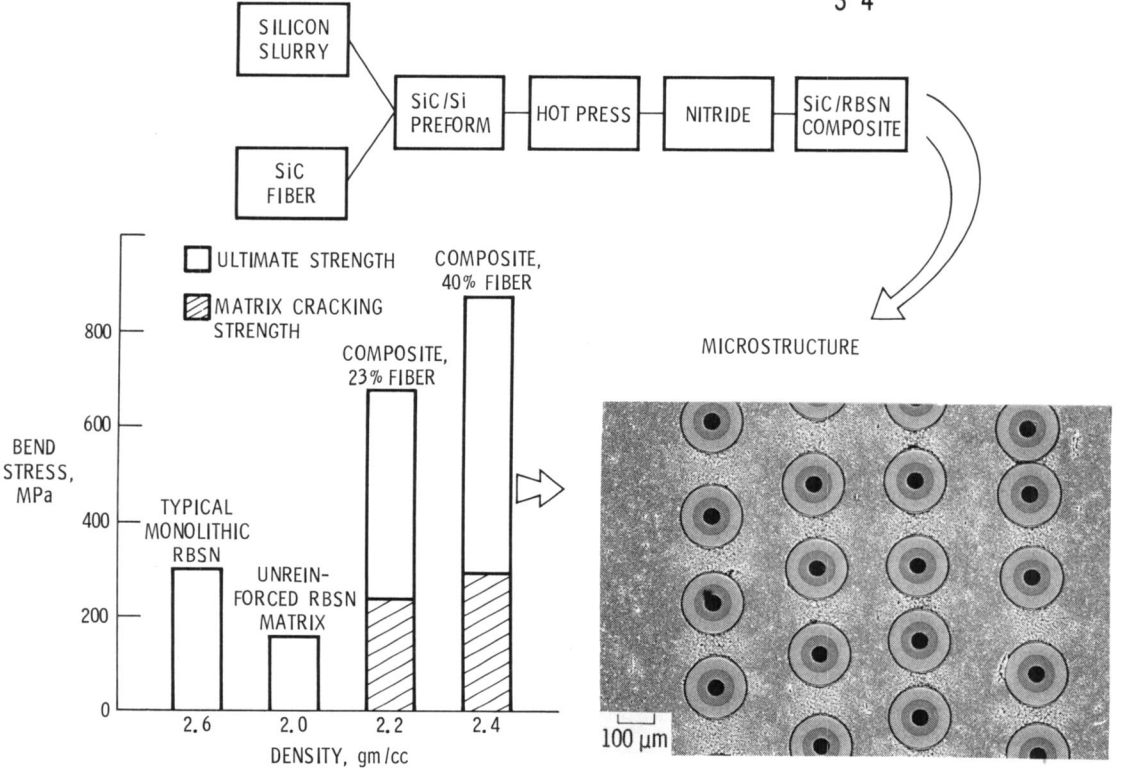
CD-85-16640

CS-85-2225

FRACTURE SURFACE OF SiC/RBSN IN TRANSVERSE FLEXURE



SiC FIBERS STRENGTHEN AND TOUGHEN REACTION-BONDED Si_3N_4

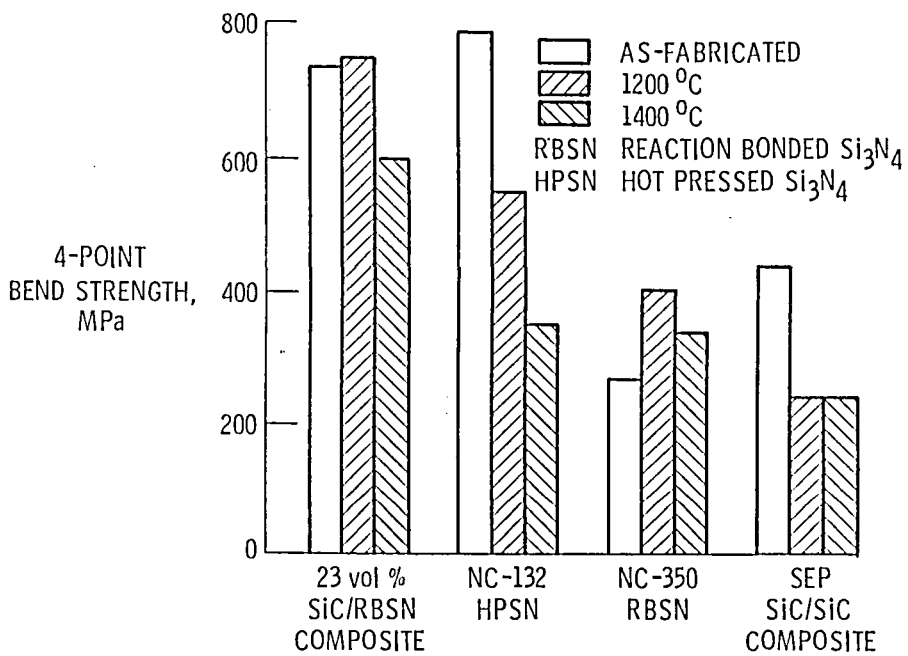


THERMAL STABILITY DATA FOR SiC/RBSN AND SiC/SiC COMPOSITES

TREATMENT	ROOM TEMPERATURE AXIAL ULTIMATE STRENGTH, MPa	
	30 vol % SiC/RBSN	SEP SiC/SiC
AS-FABRICATED	350[a]	441[b]
1200 °C, 100 hr, AIR	316[a]	234[b]
1400 °C, 100 hr, AIR	323[a]	234[b]

a-TENSILE STRENGTH.
b-4-POINT BEND STRENGTH. (NO TENSILE DATA REPORTED. TENSILE STRENGTHS WOULD BE MUCH LOWER THAN 4-POINT BEND STRENGTH.)

ELEVATED TEMPERATURE STRENGTH (4-POINT BEND) FOR SiC/RBSN COMPOSITE, MONOLITHIC SILICON-BASED CERAMICS, AND SEP SiC/SiC COMPOSITE



SUMMARY OF RESULTS

- A STRONG AND TOUGH CERAMIC MATRIX COMPOSITE CAN BE FABRICATED BY REINFORCING RBSN BY HIGH MODULUS, HIGH STRENGTH, CONTINUOUS LENGTH CVD SiC FIBER
- REINFORCEMENT OF RBSN BY CVD SiC FIBERS ALSO MEASURABLY INCREASES COMPOSITE MODULUS AND THE COMPOSITE STRESS AT WHICH MATRIX CRACKS
- WEAK FIBER-MATRIX BONDING ALLOWS MULTIPLE CRACKING AND GRACEFUL FAILURE
- COMPOSITE IS THERMALLY STABLE AND HAS BETTER ELEVATED TEMPERATURE STRENGTH THAN MANY COMMERCIALLY AVAILABLE MONOLITHIC CERAMICS
- FURTHER IMPROVEMENTS IN COMPOSITE PROPERTIES ARE POSSIBLE WITH
  - INCREASE IN MATRIX STRENGTH (DECREASE IN POROSITY)
  - SMALL DIAMETER FIBERS
  - FIBER COATING

CURRENT AND FUTURE STUDIES

CURRENT:

- OPTIMIZATION OF PROCESSING VARIABLES
- POST FABRICATION TREATMENTS
- LAMINATE PROPERTIES ($0^0/90^0$, $0^0/90^0/45^0$)
- INTERFACIAL REACTION KINETICS

FUTURE:

- MEASUREMENT OF ELEVATED TEMPERATURE TENSILE STRENGTH AND STRESS RUPTURE DATA
- THERMAL PROPERTIES
- OXIDATION

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16. Abstract

This publication is a compilation of abstracts and slides of papers presented at the NASA Lewis Structural Ceramics Workshop held at the Sheraton Hopkins Hotel, Cleveland, Ohio, on May 20 and 21, 1986. Collectively, these papers depict the scope of NASA Lewis' structural ceramics program. Each paper provides a brief overview of a technical area in which NASA Lewis Research Center has a significant research focus. The technical areas include monolithic SiC and Si_3N_4 development, ceramic matrix composites, tribology, design methodology, nondestructive evaluation (NDE), fracture mechanics, and corrosion.

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